

Pulsed laser deposition of $Y_3Al_5O_{12}:Tb$ photoluminescent thin films

G. A. Hirata,^{a)} O. A. Lopez, L. E. Shea, J. Y. Yi, T. Cheeks, and J. McKittrick
Department of Applied Mechanics and Engineering Sciences and Materials Science Program, University of California at San Diego, La Jolla, California 92093-0411

J. Siqueiros and M. Avalos-Borja
Instituto de Física-UNAM, Laboratorio Ensenada, Ensenada, B.C., C.P. 22860, México

A. Esparza and C. Falcony
Centro de Investigación y Estudios Avanzados del IPN, Departamento de Física, 07300 D. F., México

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Transparent-photoluminescent $Y_3Al_5O_{12}:Tb$ (YAG:Tb) thin films were deposited on single-crystalline sapphire at two different substrate temperatures by means of the pulsed laser deposition technique. The ablation targets were fabricated from YAG:Tb powders obtained with a new ceramic processing technique (combustion synthesis). A KrF excimer laser with an ultraviolet wavelength of 248 nm was used to evaporate the target and to grow the films. Analysis and characterization of the films were performed by scanning electron microscopy, x-ray diffraction, Auger electron spectroscopy, and photoluminescence measurements. As-deposited films were amorphous and deficient in oxygen as compared to the target. Additionally, these films were not luminescent. Postannealing treatments in air for at least 1 hr in the range 800–1200 °C were found to be necessary in order to induce crystallization and oxygenation in the films thus recovering the green photoemission of YAG:Tb with these treatments. © 1996 American Vacuum Society.

I. INTRODUCTION

During the last few years special attention has been paid to yttrium aluminum garnet [$Y_3Al_5O_{12}$, (YAG)]-based phosphors doped with rare-earth ions (Eu, Tm, Tb) due to their potential applications as luminescent layers in flat panel displays (FPDs), electroluminescent (EL) devices, and ac plasma (ACP) panels.^{1,2} A new emerging technology, pulsed laser deposition (PLD), offers great advantages over many other physical vapor deposition (PVD) and/or chemical vapor deposition (CVD) techniques because it can be used to produce high purity materials in the form of thin films. The main feature of the PLD method is the excellent stoichiometry transfer from complex inorganic compound targets and the homogeneity and uniformity over limited areas.³ Thin films of terbium-doped oxide phosphors like YAG:Tb and YAGG:Tb (yttrium aluminum gallium garnet) have already been studied and proposed for practical applications.^{1,4} Greer *et al.* used PLD for the first time to obtain YAGG:(Eu, Tb, Tm) for high luminance (brightness) thin film CRTs displays. However the substrates had to be postannealed at relatively high temperatures (>1500 °C) for several hours (>10 hr)⁴ to achieve maximum light output. Thus, from a technological point of view it is highly desirable to develop methods to obtain photoluminescent devices using lower postannealing temperatures.

II. EXPERIMENTAL TECHNIQUES

In this work we obtained YAG:Tb transparent-photoluminescent thin films grown by pulsed laser ablation.

The films were deposited on sapphire at either 300 or 400 °C substrate temperatures and postannealed at low temperatures (800–1200 °C). The YAG:Tb targets were prepared by combustion synthesis of yttrium nitrate, aluminum nitrate, and terbium nitrate. Combustion synthesis is a promising technique for phosphor synthesis because of its success in producing high quality oxide ceramic powders at considerably lower temperatures and with reduced processing time compared with conventional synthesis techniques.^{5,6}

Combustion synthesis involves the exothermic reaction of an oxidizer such as metal nitrates, and an organic fuel, typically urea (CH_4N_2O) or carbonylhydrazide (CH_6N_4O). The combustion reaction is initiated in a muffle furnace at temperatures of 500 °C or less (much lower than the phase transition of the target material). The chemical energy released from the exothermic reaction between the metal nitrates and fuel can rapidly heat the system to high temperatures (>1600 °C) and sustain these high temperatures without an external heat source. In a typical reaction, the mixture of metal nitrates decomposes, dehydrates, and ruptures into a flame after about 3–5 min.⁵ A porous, voluminous powder that can be crushed to 1–3 μm size powders with mortar and pestle is obtained.

Combustion synthesized YAG:Tb powders were cold pressed in a steel die to obtain pellets 30 mm in diameter and 3 mm in thickness. The pellets were sintered at 1000 °C for 1 hr to obtain structurally robust targets (85% dense).

YAG:Tb thin films were evaporated in a laser ablation ultrahigh vacuum system with a base pressure of 5×10^{-10} Torr. Sapphire substrates were maintained at either 300 or 400 °C during the growth of the films. A KrF excimer laser with an ultraviolet (UV) wavelength of 248 nm, 30 Hz rep-

^{a)}Present address: Instituto de Física-UNAM, Laboratorio de Ensenada, Apdo. Postal 2681, Ensenada, B.C. 22860, México.

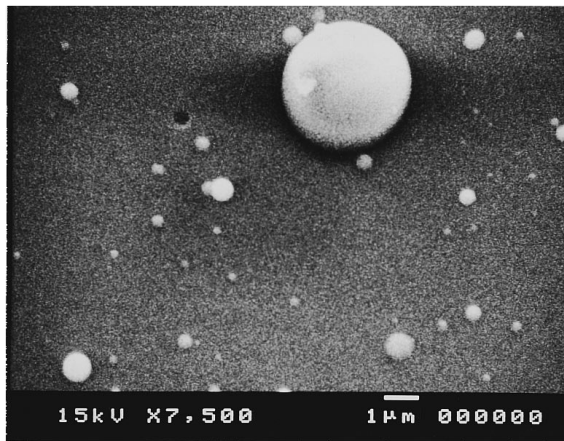


FIG. 1. Representative SEM micrograph of $Y_3Al_5O_{12}:Tb$ thin film grown on sapphire at a 400 °C substrate temperature.

etition rate, and an energy density of 3 mJ/cm^2 was focused onto the target. The as-deposited substrates were cut into small samples of about 1 cm^2 and annealed in air between 800 and 1200 °C for at least 1 hr.

The surface morphology and atomic concentration were characterized by using a scanning electron microscope (SEM) and a scanning Auger microscope (SAM). The samples were analyzed by x-ray diffraction (XRD) spectroscopy equipped with a Co excitation source ($\lambda = 1.7902 \text{ \AA}$).

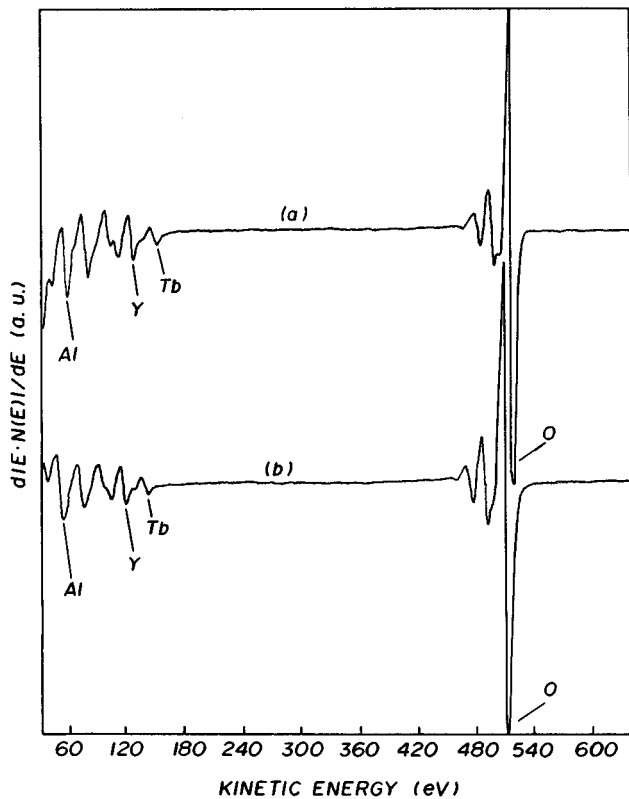


FIG. 2. Auger spectrum taken on (a) the original surface of a YAG:Tb target and (b) the surface of the same film as in Fig. 1.

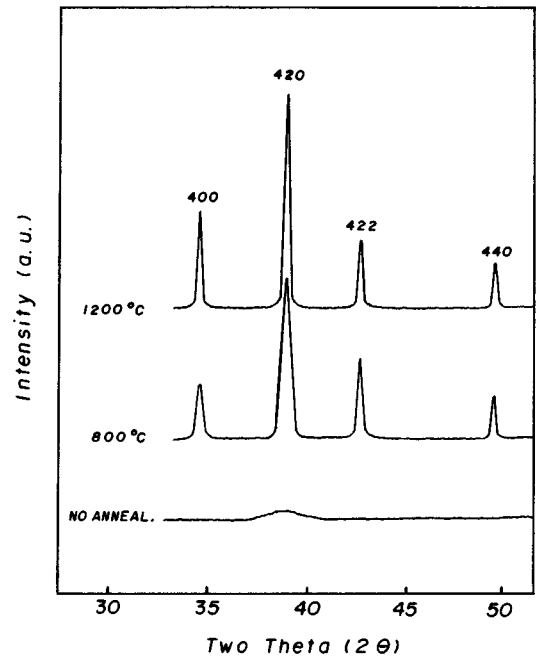


FIG. 3. X-ray diffraction patterns of three YAG:Tb thin films grown on sapphire at a 400 °C substrate temperature: (a) no annealing, (b) annealed at 800 °C, and (c) annealed at 1200 °C.

Photoluminescence (PL) characteristics of the YAG:Tb films were measured with a commercial luminescence spectrophotometer using an UV excitation radiation of 250 nm wavelength. The spectra were measured with a 290 nm filter to block out the excitation signal. The final spectra were a result of an average over five scans at 360 nm/min in the 350–650 nm range.

III. RESULTS AND DISCUSSION

The surface morphology as determined by SEM is shown in Fig. 1. It is observed that spherical particles appeared on the smooth surface of the YAG:Tb film. The chemical composition of these particles determined by AES was similar to the original target; however, on the smooth surface of the film a different stoichiometry was measured, as will be discussed below. These rounded particles of different sizes that are formed from local melting and ejected from the target to the substrate are typically found in laser ablation experiments,⁷ and can be easily removed from the surface.

The Auger spectrum in Fig. 2(a) corresponds to the original surface of the YAG:Tb target. Figure 2(b) shows a representative Auger spectrum of a YAG:Tb thin film annealed at 1200 °C for 1 hr. In both cases, the intensities of the Auger peaks for Al, Y, Tb, and O are similar, indicating that the atomic concentration of each chemical element is the same. However, the as-deposited films showed a reduction in oxygen as compared to the ablated target. Thus, annealing treatments are necessary to re-oxygenate the films to the point that YAG:Tb films recover the initial photoluminescent characteristics of the target.

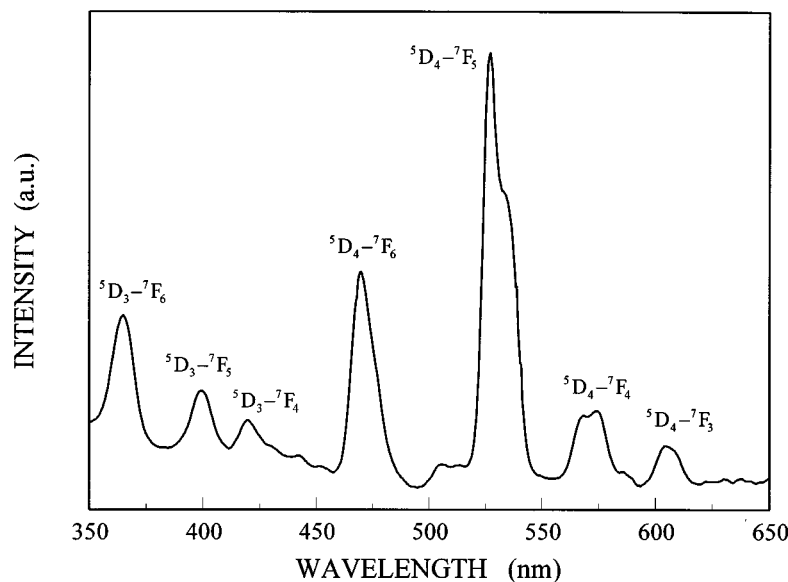


FIG. 4. Photoluminescence of $Y_3Al_5O_{12}:Tb$ thin film grown on sapphire at 400 °C and subsequently annealed at 1200 °C for 1 hr.

The effect of the annealing temperature on the structure of deposited films measured by XRD is shown in Fig. 3. As the temperature is raised, the intensity of the diffraction peaks increases. For the as-deposited film, a small, broad peak is detected. After annealing at 800 or 1200 °C diffraction peaks appear with different relative intensities and correspond to crystallographic planes of the $Y_3Al_5O_{12}$ structure excited with a Co x-ray source ($\lambda=1.7902 \text{ \AA}$). We also observed from Fig. 3 that grain size for films annealed at higher temperatures (1200 °C) is larger than that annealed at 800 °C (narrower peak widths).⁸

Figure 4 shows a representative photoluminescence spectrum of a YAG:Tb thin film annealed at 1200 °C for 1 hr. As reported by Chase *et al.*⁹ and Khang,¹⁰ the main peak of green emission at 545 nm corresponds to $^5D_4-^7F_5$ transitions arising from the (4*f*) electron configuration of a Tb^{3+} ion. The other peaks labeled indicated in Fig. 4 are also attributed to different transitions in terbium.¹¹ This spectrum is identical to the YAG:Tb⁺³ photoluminescence spectrum reported by other work.^{9,10,12}

IV. CONCLUSIONS

In this work photoluminescent YAG:Tb thin films were evaporated by pulsed laser deposition on monocrystalline sapphire substrates. The ablated targets were prepared by combustion synthesis of (Y,Al,Tb) nitrates in a muffle furnace maintained at 500 °C.

As-deposited films were amorphous and deficient in oxygen as determined by x-ray diffraction and Auger spectroscopy

and were not luminescent. Postannealing treatments in air for at least 1 hr in the range of 800–1200 °C were found to be necessary in order to re-establish photoluminescence on the films by crystallization and re-oxygenation. In our experiments, similar results were obtained for films deposited at the two different substrate temperatures, 300 or 400 °C.

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¹J.A. Greer, H.J. Van Hook, M.D. Tabat, H.Q. Nguyen, G. Gammie, and P.F. Koufopoulos, *Mater. Res. Soc. Symp. Proc.* **345**, 281 (1994).

²S.W. Depp and W.E. Howard, *Sci. Am.* **267**, 90 (1993).

³G.K. Hubler, *MRS Bull.* **26** (1992).

⁴J.A. Greer, H.J. Van Hook, H.Q. Nguyen, M.D. Tabat, G. Gammie, and P.F. Koufopoulos, *SID Proc.* **35**, 827 (1994).

⁵L.E. Shea, J. McKittrick, and O. A. Lopez, *J. Am. Ceram. Soc.* (submitted).

⁶J.J. Kingsley and K.C. Patil, *Mater. Lett.* **6**, 427 (1988).

⁷*Pulsed Laser Deposition of Thin Films*, edited by D.B. Chrisey and G.K. Hubler (Wiley, New York, 1994).

⁸B.H. Choi, H.B. Im, J.S. Song, and K.H. Yoo, *Thin Solid Films* **193/194**, 712 (1990).

⁹E.W. Chase, R.T. Hepplewhite, D.C. Krupka, and D. Kahng, *J. Appl. Phys.* **40**, 2512 (1969).

¹⁰J.D. Kahng, *Appl. Phys. Lett.* **13**, 210 (1992).

¹¹W.F. van der Weg and M.W. van Tol, *Appl. Phys. Lett.* **38**, 705 (1981).

¹²W.F. van der Weg, Th. J.A. Popma, and A. T. Vink, *J. Appl. Phys.* **57**, 5450 (1985).