

Cathodoluminescence Study of Gadolinium-Doped Yttrium Oxide Thin Films Deposited By Radio-Frequency Magnetron Sputtering

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Abstract

A multi-layer gadolinium-doped yttrium oxide thin film was deposited in a combinatorial fashion on a Si (001) substrate using radio-frequency magnetron sputtering. Alternating layers of Y_2O_3 and Gd were deposited for a total of 9 layers. The film was homogenized in composition by an 850 °C 12 hour thermal treatment producing a range of composition from $Y_{1.96}Gd_{0.04}O_3$ – $Y_{1.54}Gd_{0.46}O_3$ in a single film. Ultraviolet emission with a peak wavelength at 314-315nm was observed from the gadolinium $^8S_{7/2}$ - $^6P_{7/2}$ transition via cathodoluminescence (CL) excitation. The CL-induced intensity was found to be maximum at 9 at% Gd ($Y_{1.82}Gd_{0.18}O_3$) and an optimized electron probe of $V_{acc} = 13$ keV was determined for the 1 μ m thick thin film. Gadolinium activator saturation was observed for sample current density greater than 0.03 μ A/cm². Non-radiative decay via thermal pathways is suspected for the observed activator saturation.

Introduction

Miniaturized ultraviolet (250 – 350 nm) emitting solid-state sources are required as components for proposed device structures such as non-line-of-sight communication transceivers and receivers and bio-particle detection units. Previous work on rare-earth doped yttrium oxide materials have shown emission from the blue to red range of the electromagnetic spectrum from trivalent Pr, Sm, Eu, Tb, Dy, Er, Ho, and Tm [1–2]. We have recently determined that gadolinium-doped yttrium oxide powder exhibits intense emission at ~ 314 – 315 nm. In this paper we will report work on gadolinium-doped yttrium oxide (also yttria and yttria sesquioxide) *thin films* that are being explored as a potential material for thin film solid-state UV device applications.

Background and Experimental

Gadolinium-doped, yttrium oxide thin films have been prepared by combinatorial sputtering using a radio-frequency magnetron sputtering system (AJA international, ATC 2000 – V). The magnets supporting the sputter targets were operated in an unbalanced mode to maximize the deposition rate. The magnetron system used has a “sputter-up” configuration, where the substrate surface is located above two sputter targets that are tilted and facing the substrate. The sputter guns are spaced 180° apart in the chamber in reference to the center of the substrate. Hence, the resulting film deposited from this configuration will have a maximum composition gradient along a line on the substrate surface.

Gadolinium foil (0.024 in thick, Alfa Aesar) and a yttrium metal target (0.250 in. thick, Kurt J. Lesker), both 99.9% pure, were used as sputtering targets. During deposition, the gadolinium target was operated at 100 W forward power, and the yttrium target was operated at 200 W. The combinatorial film was deposited in a multi-layer fashion; 9 alternating layers, Y_2O_3 – $[Gd - Y_2O_3]_4$ were deposited onto Si (001). The Si wafer was 4 in. in diameter, research grade, boron doped, and with 14 – 22 Ω -cm resistivity. The total pressure during sputtering was

$P_T = 3$ mTorr when depositing both the Gd and Y_2O_3 film layers. The yttrium oxide was reactively sputtered in metallic mode with a self-bias of 440 V. The oxygen was delivered preferentially at the substrate surface to react with sputtered metallic yttrium atoms to form the yttrium oxide thin film. The ratio of the oxygen to argon flow rates of 0.074 was used, though a higher oxygen partial pressure is realized at the substrate due to the localized oxygen injection. The gadolinium metal layers were sputtered in pure argon with a self-bias of 401 V. The distance from the center of the 2" sputter target to the near and far edge of the 6" substrate holder was 12 and 20", respectively.

Combinatorial *multi-layers* of alternating yttria–gadolinium were deposited and the gadolinium dopant was subsequently driven into the yttria via a post–deposition thermal treatment at 850 °C for 12 hours. This post-deposition anneal is critical to enhance the crystalline quality of the film which is critical to luminescence because the defect structure within the lattice dictates the luminescence behavior. Yttrium atoms can be embedded in one of two possible sites in the yttrium oxide lattice, both of which are defined by the defect structure surrounding them. The yttrium atom resides as the body–centered atom in a body–centered cubic lattice position surrounded by eight oxygen atom sites, two of which are vacant [3-4]. Oxygen vacancies order in the unit cell either as a pair along a face diagonal (no inversion symmetry) or as a pair along a body diagonal (inversion symmetry) with respect to the central yttrium atom [3-4]. The yttrium embedded in an inversion symmetry environment is labeled C_{3i} and the site without this element of symmetry C_2 .

The Gd^{3+} dopant occupies yttrium positions in the yttria lattice and retains most of its atomic electronic nature, even when embedded in the yttria crystal field, due to screening of the 4f–4f intra-shell transition by the filled 5s and 5p shells. Moreover, this 4f–4f transition is forbidden because the parities of the initial and final states are the same. However, this restriction is partially lifted when Gd^{3+} occupies yttrium lattice sites devoid of inversion symmetry, i.e., the C_2 site. This site is in 75% abundance relative to the C_{3i} site [4]. Hence, ultraviolet luminescence occurs from Gd: Y_2O_3 from screened Gd^{3+} impurities. *Ultraviolet* luminescence arises because the stable $^8S_{7/2}$ ground state is separated by more than 32 000 cm^{-1} (3.95 eV) from the lowest excited state ($^6P_{7/2}$) resulting in a high energy transition relative to the other rare–earth elements [5–6].

Cathodoluminescence (CL) studies were carried out in a JEOL 6700F scanning electron microscope equipped with energy dispersive spectroscopy (EDS) and a fully integrated GATAN MonoCL system equipped with imaging and scanning monochromator (0.2 nm resolution, 185 – 900 nm) and a LN_2 cold / hot stage operating from 80-375 K. A Gatan MonoCL3+ system was used to collect the CL data which was scanned in 2 nm steps with a collection time per step of 1 second. The sample was irradiated by the electron–beam at normal incidence using a variety of beam energies from 5–20 keV. CL measurements were taken at working distance (WD) = 8 mm and 500X magnification.

Results and Discussion

A combinatorial Gd– Y_2O_3 multi–layer film with a pre–selected composition gradient was successfully prepared in the first attempt with the aid of a program written to model the film gradient. The Matlab[®] software tool was used to compile a program that roughly predicts the combinatorial thin film composition based on a combination of experimentally obtained data; sputtering rates, deposition profiles, sputtering times, and the sputter target materials' atomic weights and densities. The sputtered flux spatial distribution at the substrate surface was calculated by careful measurements of the critical chamber dimensions such as target tilt with

respect to the substrate and target-to-substrate distance, and the flux was assumed to obey a “surface-source” evaporation model [7] with account taken for a forward-peaked, $\cos^n\phi$, distribution due to “chimneys” that shape the emerging flux from the sputter guns. In essence, the chamber dimensions and sputter model were used to determine the relative “composition profile” over the 2D substrate surface. The relative thickness was then modified by multiplication of a factor to account for sputter rate, density, atomic weight, and sputter time. Figure 1 compares the predicted at% Gd in Y_2O_3 (figure 1a) and the experimentally obtained composition profile (figure 1b). Sputtering conditions 1) yttrium sputter at 200 W (rf) metallic, reactive mode in $p_T = 3$ mTorr ($p_{O_2}/p_{Ar} = 0.074$, $Q_{Ar} = 25$ sccm Ar, 2 sccm O_2 , substrate – to – target distance 12 – 20 cm, room temperature deposit. 2) gadolinium sputter at 100 W (rf) metallic mode in $p_T = 3$ mTorr Ar, $Q = 20$ sccm Ar, substrate – to – target distance 12 – 20 cm, room temperature deposit.

The experimental profile was generated using calibrated EDS (energy dispersive spectroscopy) along a combinatorial, multi-layer thin film that was roughly homogenized by the post-deposition anneal. The EDS data was taken along an imaginary line on the substrate surface that contained the largest gadolinium concentration gradient (the parallel line between the two targets). The predicted gadolinium atomic concentration of 2 – 20 % was in excellent agreement with the measured concentration profile of 2 – 23.

The yttrium oxide thin film deposited at room temperature had a θ – 2θ x-ray diffraction pattern characteristic of yttria powder. The film was polycrystalline with very little x-ray signal indicating a low degree of crystallinity following deposition. However, after the post-process anneal the (222) pole of the doped yttrium oxide film was the prominent reflection along the surface normal of the substrate. For example, the integrated intensity ratio for the (222) to the (400) reflection for yttria powder is 4 [8]. Following the thermal treatment the film had a ratio of 750. The preferred orientation is most probably due to the fact that the (111) plane in yttrium oxide has the lowest surface free energy in the yttrium oxide unit cell [9].

The yttria thin film sputtering parameters were optimized prior to CL experiments in order to obtain high quality film. The thin film quality was measured by x-ray diffraction experiments. The film processing partial pressure ratio of $P_{O_2}/P_{Ar} = 0.074$, at $P_T = 3$ mTorr, produced the largest integrated intensity for the (222) reflection, characteristic of yttrium oxide formation, over the range $P_{O_2}/P_{Ar} = 0.06$ – 0.084 . At $P_{O_2}/P_{Ar} < 0.06$ a yttrium peak in a θ – 2θ scan indicated yttrium metal was being deposited and the yttrium–oxygen reaction was oxygen mass transport limited. For $P_{O_2}/P_{Ar} > 0.084$, the sputtering mode changed from metallic, reactive mode, to oxide mode, which greatly reduced the sputtering rate.

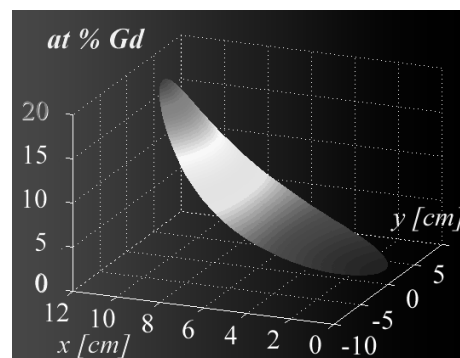


Figure 1a Simulation of the at% Gd in a combinatorial, multi – layer thin film, $Y_{2-x}Gd_xO_3$.

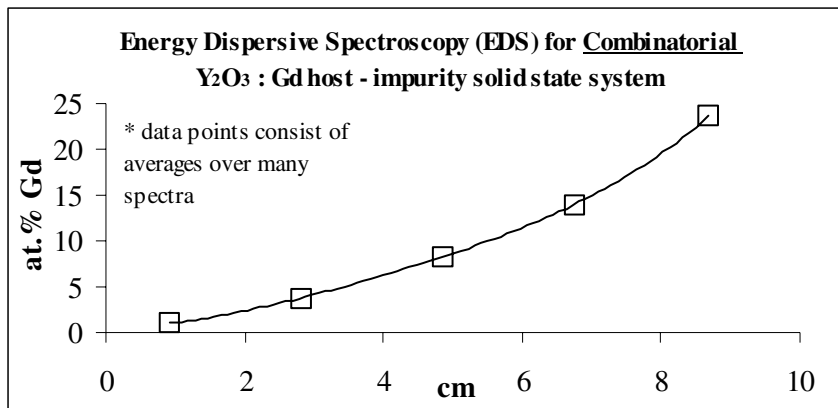


Figure 1b EDS of film prepared under conditions listed in figure 1a + 850 °C, 12 hour anneal to homogenize Gd concentration

CL measurements were made at constant beam accelerating voltage ($V_{acc} = 15$ kV) and constant beam sample current (30 – 35 pA), along the length of the prepared yttria-Gd film, to determine the optimum atomic % Gd. The plot of the integrated intensity of the 314 – 315 nm peak vs. atomic % Gd is shown in figure 2. The maximum intensity occurs at ~ 9 at% Gd. The maximum intensity is in good agreement with the peak concentration of 12 at% Gd for gadolinium doped yttria *powders* [10]. The initial intensity increases as the atomic % Gd increases because the density of gadolinium cations available for excitation increases. Beyond 9 atomic % Gd, the intensity of the 314 – 315 nm signal begins to decrease which is indicative of concentration quenching. The probability of concentration quenching increases as the gadolinium concentration increases because the average activator ion distance (Gd–Gd) decreases in the host. As this distance decreases the probability of dipole or quadrupole interaction between the ions increases due to wave function overlap. Because of the wave function overlap a trapped carrier can hop between Gd ions and as the hopping frequency increases with decreasing spacing the charges can be trapped by a non-radiative center.

Hence, the non-radiative recombination becomes more probable at high concentration, reducing the Gd:Y₂O₃ quantum efficiency η ;

$$\eta = \frac{W_R}{W_R + W_{NR}}$$

where W_R is the radiative recombination probability and W_{NR} is the non-radiative recombination probability.

Figure 3 shows a plot of the integrated CL peak intensity versus electron beam energy of 9 atomic % Gd yttrium oxide thin film. This plot is in good agreement with Monte Carlo simulations performed to determine the optimum fit of the electron interaction volume to the yttrium oxide film thickness. The average film thickness for the combinatorial/multilayer film was 1 μ m. At $V_{acc} = 13$ keV, the electron interaction volume in the thin film reaches within 0.1 μ m of the yttria–silicon substrate interface. CL excitation takes place most efficiently at the end of the electron interaction range. Consequently to optimize the CL efficiency, it is critical maximize the electron energy range in the activated material. Carriers generated at the perimeter of this excitation volume are expected to diffuse through the film and trap at activator sites to

radiatively recombine. The optimum interaction volume occurs at $V_{acc} = 13$ keV; at 12 keV the interaction volume does not penetrate fully into the $1\ \mu\text{m}$ film and at 14 keV the interaction volume begins to penetrate the yttria-Si interface.

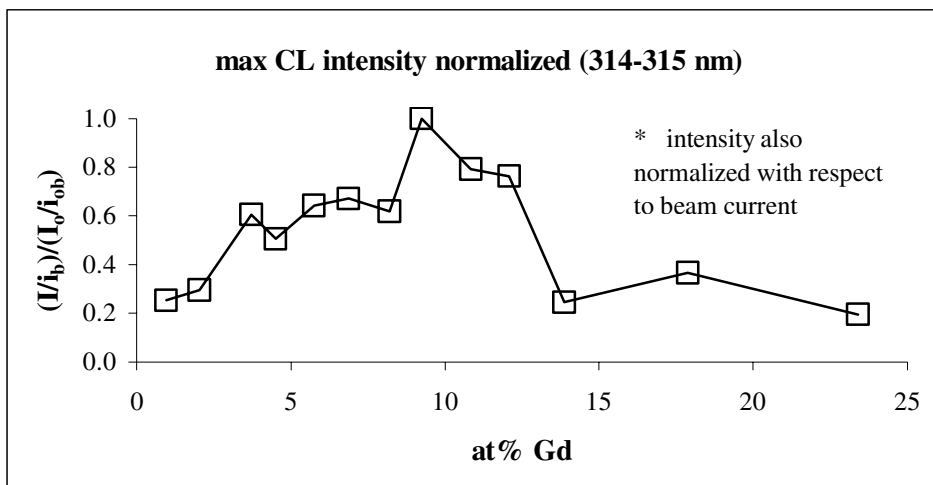


Figure 2 CL intensity at 314 – 315 nm vs. at% Gd. The intensity has been normalized with respect to beam current. The current changed only slightly over from 30 – 35 pA. $V_{acc} = 15\text{keV}$

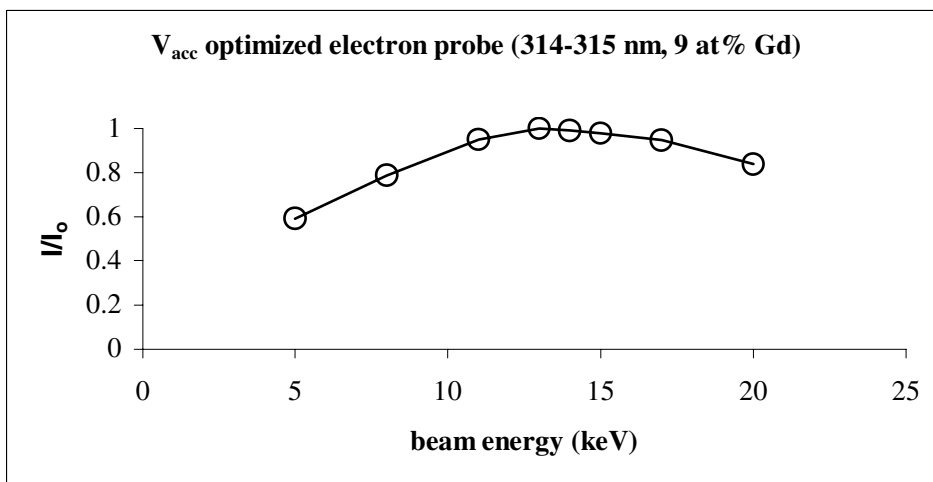


Figure 3 The optimum electron probe voltage for a $1\ \mu\text{m}$ thick $\text{Gd:Y}_2\text{O}_3$ film was 13 keV.

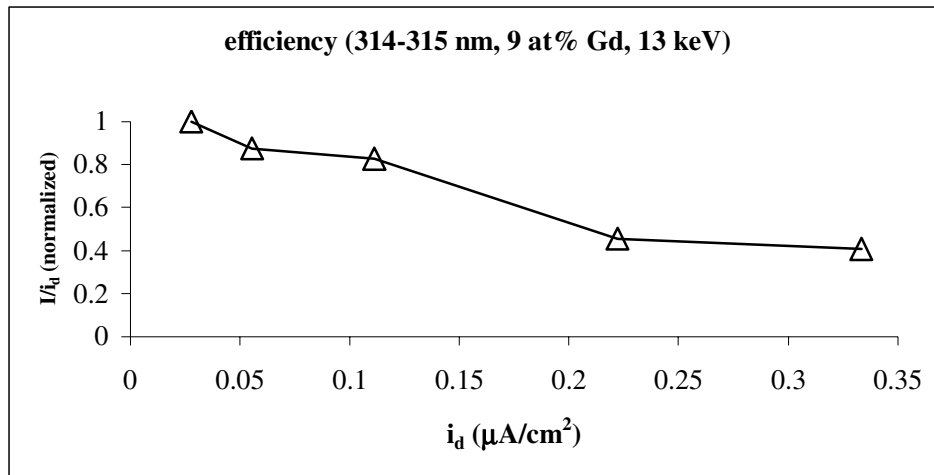


Figure 4 A plot of intensity/ current density vs. current density decreases over the current density range probed (60 pA – 700 pA) indicating saturation.

Figure 4 is a plot of the normalized CL efficiency vs. current density, which indicates a steady decrease in CL efficiency as current density is increased. This result indicates current saturation of activator ions over the range of current density shown. Ground-state depletion and/or beam-heating effects are typically responsible for the current saturation effects [2]. In the Gd-doped yttrium oxide, ground state depletion seems less likely because the density of electrons within the irradiated volume is six orders of magnitude less than the density of activator ions. Even when a smaller effective CL volume is taken into consideration the number of Gd ions is still significantly more than the number of electrons. A correlation of the temperature dependent CL intensity and the effective temperature rise due to beam heating will be performed to elucidate the current saturation behavior.

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