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2002 J. Phys. D: Appl. Phys. 35 433

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J. Phys. D: Appl. Phys. **35** (2002) 433–438 PII: S0022-3727(02)31933-8

Optical and luminescent properties of undoped and rare-earth-doped Ga_2O_3 thin films deposited by spray pyrolysis

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Received 17 December 2001
Published 20 February 2002
Online at stacks.iop.org/JPhysD/35/433

Abstract

Spray pyrolysis was used to prepare polycrystalline thin films of undoped Ga_2O_3, as well as those doped separately with Eu^{3+}, Tb^{3+} and Tm^{3+}. The energy gap values of the as-grown films and those annealed at 600˚C and 900˚C were found to be 4.75, 4.48 and 4.44 eV, respectively. Films containing Eu^{3+} and Tb^{3+} exhibited red and green cathodoluminescence (CL), respectively. The CL of $Ga_2O_3:Tm$ mainly showed a broad band in the blue–green region, which resulted from the emission by both the Ga_2O_3 host and Tm^{3+}. The broad blue–green emission band was divided into three Gaussian peaks at 424 nm (2.92 eV), 497 nm (2.49 eV) and 526 nm (2.36 eV). The CL intensity of undoped Ga_2O_3 thin films depended on the annealing ambient and temperature, suggesting that it is associated with the presence of oxygen vacancies. Mechanisms responsible for the broad blue–green emission of undoped Ga_2O_3 thin films were explored.

1. Introduction

Monoclinic gallium oxide (β-Ga_2O_3) is a wide-band gap compound. The optical band gap of single-crystal β-Ga_2O_3 has been measured to be 4.2–4.9 eV [1–3]. The conductivity of single-crystal β-Ga_2O_3 can vary from insulator to conductor, depending on the preparation conditions [4]. Due to its varied optical and electronic properties, β-Ga_2O_3 has been used for a wide variety of applications such as optical window [5], high temperature chemical gas sensor [6], magnetic memory [7], and dielectric layer [8]. Recent reports include novel optical and photoluminescent (PL) properties in nanowires and quantum wells [9, 10]. Most of the reported optical and electronic properties of β-Ga_2O_3 are based on single-crystal or other bulk structures.

Recently, β-Ga_2O_3 has attracted interest as a phosphor host material for applications in thin film electroluminescent (TFEL) displays [11, 12]. Since it is extremely stable chemically and thermally, β-Ga_2O_3 may emerge as an alternate choice to sulfide-based phosphors. Thin films of Ga_2O_3 have been prepared by a sol-gel process, and PL and TFEL behaviour of this host material has been described for multicolour-emitting phosphors [11]. Its luminescent properties without dopants has not received much attention. Recently, Ga_2O_3 thin films were prepared by the ultrasonic spray pyrolysis method using gallium acetylacetonate as source material and water as oxidizer, the luminescent properties were not studied [13]. Further, there appear to be no reports of the cathodoluminescent (CL) properties of Ga_2O_3 thin films. In our previous work, spray pyrolysis has been used to prepare a variety of thin films of oxide phosphors such as Y_2O_3 and $Sr_2B_5O_9Cl$ [14, 15]. In the present paper, we report the use of this technique to deposit thin films of undoped and rare-earth-doped β-Ga_2O_3. Optical absorption and the luminescent characteristics of these films are presented.

2. Experimental set-up

Thin films of undoped and rare-earth-doped Ga_2O_3 were deposited by spray pyrolysis on a variety of substrates including Corning 7059 glass, quartz and aluminosilicate ceramic plates. To prepare thin films of undoped Ga_2O_3, the spray pyrolysis solution contained 0.1 M $Ga(NO_3)_3$ (5 N, Alfa). For the rare-earth-doped Ga_2O_3 films, a stock solution of 0.1 M $Ga(NO_3)_3$ was mixed in appropriate ratios with separate solutions of $Eu(NO_3)_3$, $Tb(NO_3)_3$ and $Tm(NO_3)_3$ to provide spray solutions containing 1.0 at% of rare-earth dopants relative to gallium. The spray was developed by an ultrasonic nebulizer and was directed towards the substrate by a carrier gas of humid air at a flow rate of 1.2 L min^{-1}. The spray chamber made of Pyrex glass was mounted on an x–y translation table to raster the aerosol over an area of 2.5 × 5.0 cm^2. The deposition temperature was 400˚C. After deposition, some samples were annealed in a variety of ambients, including air, nitrogen, argon, and forming gas ($H_2 : N_2 = 5 : 95$). Various annealing temperatures up to 900˚C were provided by a tubular oven using a ramp rate of 30˚C min^{-1}.

The crystal structure and phase were identified using a Rigaku Geigerflex II x-ray diffractometer (XRD) with Co Kα radiation. The JCPDS database and powercell diffraction pattern simulation software were used for phase identification. The morphology of the films was determined by a Hitachi S570 scanning electron microscope (SEM). The composition of the samples was analysed by energy dispersive spectroscopy (EDS) using the Voyager II 1100 x-ray microanalysis system attachment of the SEM. Optical absorption spectra of the films on quartz were recorded at room temperature using a Shimadzu UV 160U spectrometer with a blank piece of quartz glass in the reference beam. A mercury arc lamp along with a monochromator was used as the excitation source for PL measurement. The CL emission was obtained using a home-made system based on a CL luminoscope (Relion Industries ELM-2B) with a cold cathode electron gun. The CL spectra were measured using an Ocean Optics S2000 CCD spectrometer with a 400 μm diameter single-strand UV/VIS optical fibre. Spectral resolution of the spectrometer was 1.5 nm. Loading several samples on the sample holder, which was controlled by an x–y positioner, facilitated measuring the emission of the samples in sequence under the same conditions. A metal mask with a 3 mm diameter hole was placed on each sample to define the emitting spot. Typical conditions consisted of a beam voltage of 5 kV and a beam current of 0.5 mA in a vacuum chamber (20–60 mTorr). Due to the beam scattering in the chamber, the effective current density on the sample was measured to be 62 $\mu A\,cm^{-2}$ under the typical condition. A Minolta T-1M illuminance meter was used to measure the luminance of the films.

3. Results and discussion

3.1. Crystal structure and morphology

Figure 1 shows the XRD spectra of Ga_2O_3 films deposited onto quartz substrates held at 400˚C. Bulk gallium nitrate is known to decompose to form Ga_2O_3 at 200˚C [16]. Furthermore, the decomposition temperature for the pyrolysis solution may be lower relative to the bulk material, since the pyrolysis mixture consists of dissolved ions and water. Consequently, gallium nitrate was expected to be converted completely to Ga_2O_3 during spray pyrolysis at 400˚C. Figure 1(*a*) illustrates that the as-grown film was either amorphous or consisted of very small crystallites. Thin films after heat treatment in air formed a polycrystalline structure as shown in figure 1(*b*) and (*c*). Comparison of the observed *d* values with standard *d* values from JCPDS data card number 41-1103 showed a mixed orientation, primarily (111) and (−310) of a monoclinic type structure. In addition, the film annealed at 900˚C exhibited enhanced crystallinity relative to the film annealed at 600˚C. However, on comparing our previous studies of Y_2O_3 and WO_3 films [14, 17], the lines of XRD spectra of Ga_2O_3 films were less intense under similar annealing conditions.

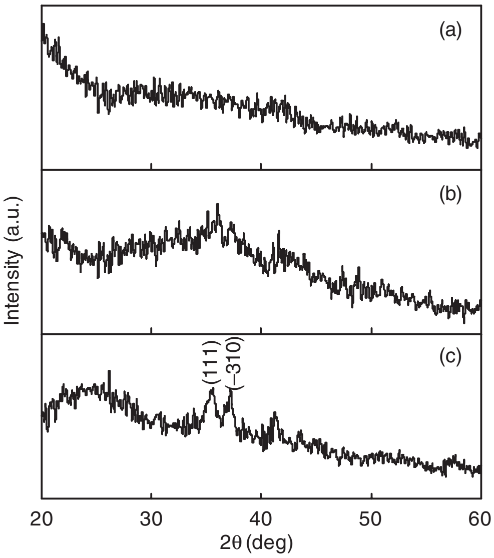

Figure 1. X-ray diffraction patterns of Ga_2O_3 thin films grown on quartz substrates held at 400˚C: (*a*) as-grown; (*b*) annealed at 600˚C for 1 h; (*c*) annealed at 900˚C for 1 h.

The SEM images in figure 2 show the morphologies of β-Ga_2O_3 thin films before and after annealing. The SEM image of as-grown Ga_2O_3 film in figure 2(*a*) illustrates a branch-like morphology with a large degree of porosity and a small number of particles. Annealing in O_2 at 600˚C for 1 h caused crystallization and considerable changes in film morphology (figure 2(*b*)). Apparently, the films became denser upon annealing.

3.2. Optical absorption

Figure 3 shows the optical absorption spectra of both as-grown and annealed films at room temperature. To avoid UV absorption by Corning 7059 glass substrates, the samples were grown on quartz substrates. All samples including the as-grown film exhibited nearly the same absorption edge supporting the conclusion that deposition at 400˚C resulted in the conversion of gallium nitrate to the gallium oxide film. In addition, short wavelength absorption of the films was found to be sensitive to post-annealing temperature. This difference in optical absorption for various processing conditions was observed for other sprayed films such as $RbTiOPO_4$ thin films [18].

The energy gap E_g has generally been calculated from appropriate plots of the absorption coefficient relative to the photon energy [19]. It has been shown that Ga_2O_3 single-crystals have the direct energy band structure with anisotropic

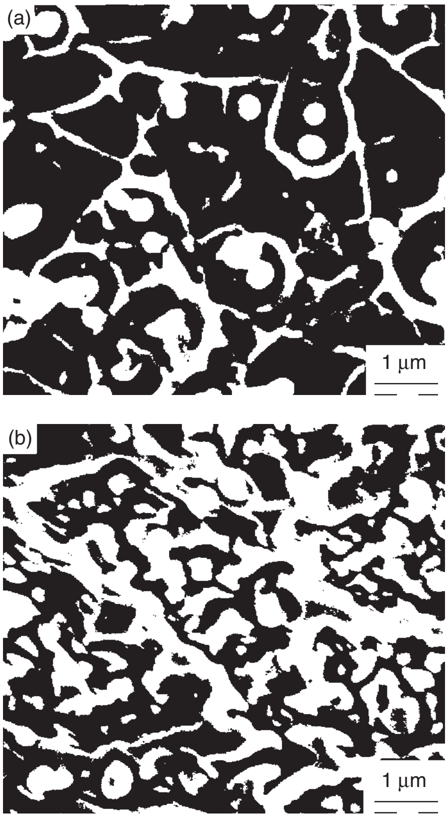

Figure 2. SEM images of Ga_2O_3 thin film deposited by spray pyrolysis (*a*) as-grown; (*b*) annealed at 600°C for 1 h.

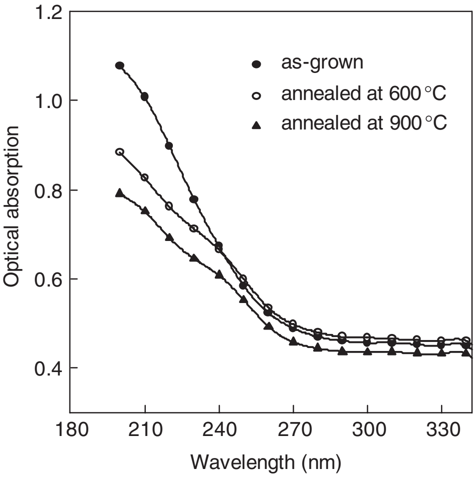

Figure 3. Optical absorption spectra of as-grown and annealed Ga_2O_3 thin films on quartz substrates at room temperature.

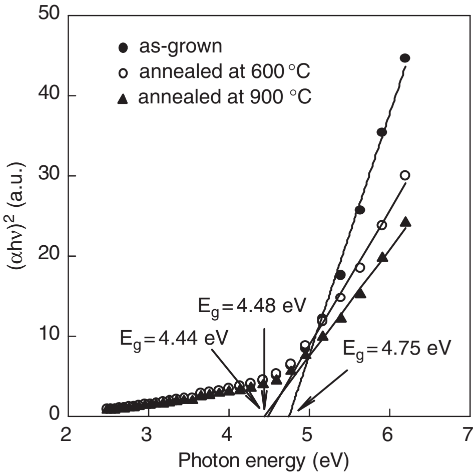

Figure 4. Plots of $(\alpha h\nu)^2$ versus the incident photon energy $h\nu$ for the as-grown and annealed Ga_2O_3 thin films. The direct energy gap values of 4.75, 4.48 and 4.44 eV were obtained for the as-grown films, annealed films at 600°C and 900°C, respectively.

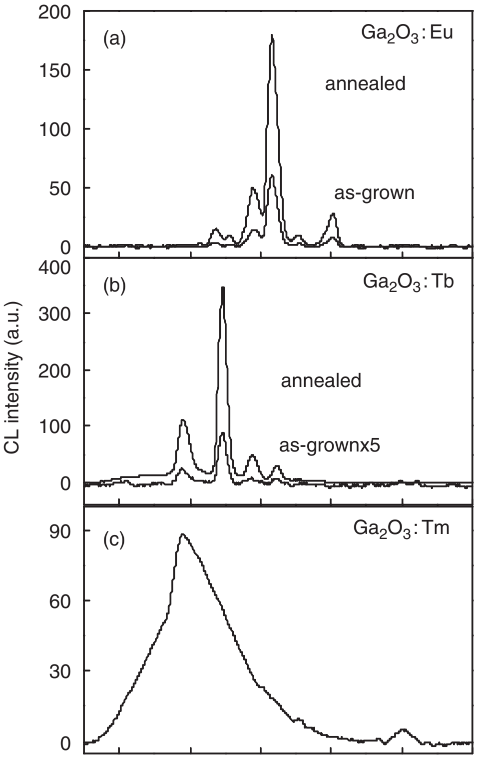

Figure 5. CL spectra for Eu-, Tb- and Tm-doped Ga_2O_3 films with a 1 at% concentration of the dopant in the spray solutions. These films were deposited at 400°C. The annealed films were heated at 600°C for 1 h in air.

optical properties [2]. Therefore, the values of $(\alpha h\nu)^2$ are plotted as a function of the incident photon energy $(h\nu)$ as illustrated in figure 4. Extrapolating the straight line portion of the plots to $(\alpha h\nu)^2 = 0$, the direct energy gap value of 4.75 eV was obtained for the as-grown films. Using the data in figure 4, energy gap values of 4.48 and 4.44 eV were also estimated for the films annealed at 600°C and 900°C, respectively. These results are in reasonable agreement with the values of energy gap reported for single-crystal, thin film and polycrystalline β-Ga_2O_3 [1–3, 5, 13]. A slight decrease in E_g of the crystallized films relative to the as-grown film was also observed for sprayed $RbTiOPO_4$ [18], and ZnO films [20].

3.3. Luminescence of rare-earth-doped Ga_2O_3 thin films

Figure 5 shows the CL spectra of Ga_2O_3 films doped separately with Eu, Tb and Tm. The substrate temperature was 400°C, and the spray solutions contained 1% dopant relative to Ga. The annealed films were heated at 600°C for 1 h in air. The CL spectra were measured at room temperature using an excitation voltage of 5 kV and a current density of 62 μA cm^{-2}. The peaks shown in figure 5(*a*) and (*b*) are characteristic of transitions between electronic energy levels of Eu^{3+} and Tb^{3+} ions, respectively. The annealing process caused an increase in the CL intensity. This improvement corresponds to the structural change of the films illustrated in figures 1 and 2. In this regard, the luminance of the annealed $Ga_2O_3 : Eu$ (red emission) and $Ga_2O_3 : Tb$ (green emission) was measured to be 27 and 41 cd m^{-2}, respectively. These values are not as large as those obtained for the red and green phosphors based on the Y_2O_3 host prepared and measured under the same conditions [14]. This is due to the poor crystallization of the Ga_2O_3 thin films as mentioned above. Earlier work indicated that the CL intensity increased as the crystallinity of the films improved [14]. Another possible reason of lower CL intensity of Ga_2O_3 thin films could be attributed to the role of oxygen vacancies in Ga_2O_3 thin films described in the following section of this paper. For the CL of $Ga_2O_3 : Tm$ shown in figure 5(*c*), it is interesting that the spectrum exhibits no sharp blue emitting peak corresponding to transitions between electronic energy levels of Tm^{3+}, while only a minor peak was obtained around 813 nm relating to the transition from $^1G_4 \rightarrow {}^3H_5$ of the Tm^{3+} ion. Instead, a broad blue–green emission occurred over the range from 350 to 650 nm. Since it is possible that this blue–green emission may still be due to transitions involving Tm^{3+} levels or that it comes from the Ga_2O_3 host, the CL of undoped Ga_2O_3 thin films was determined as described below.

3.4. *CL of undoped Ga_2O_3 thin films*

For comparison, the undoped Ga_2O_3 films were deposited and annealed under the same conditions as those for $Ga_2O_3 : Tm$ films. Figure 6 presents the CL spectrum of a Ga_2O_3 thin film measured at room temperature using an excitation voltage of 5 kV. As illustrated, the undoped film also showed a broad blue–green emission, very similar to that in Tm-doped Ga_2O_3 thin films. Furthermore, the luminance under the same conditions was 10 and 19 cd m^{-2} for the Ga_2O_3 and $Ga_2O_3 : Tm$ films, respectively. Consequently, although the undoped film exhibits a spectrum very similar to that for the Tm-doped film, the Tm dopant enhances the CL emission intensity. This emission band can be separated into three Gaussian bands as shown in figure 6. Two major emissions were centred at 497 and 526 nm, while one minor emission was centred at 424 nm. These peak positions had a slight change with the sample.

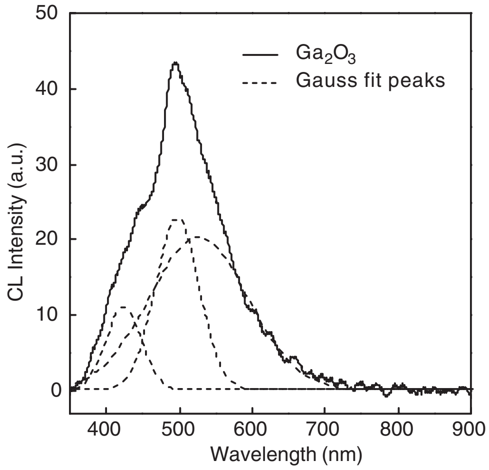

Figure 6. CL spectra (——) of undoped Ga_2O_3 thin films measured at room temperature. The broad emission can be Gaussian divided into three bands (- - - -).

Earlier studies indicated that β-Ga_2O_3 could exhibit up to three different PL bands corresponding to UV, blue and green emission, depending on the sample preparation and the nature of the dopant [21]. Among these, the green emission occurs only in the presence of specific impurities such as Be, Ge and Sn, while the blue luminescence is produced in Ga_2O_3 doped with Zr^{4+} or Si^{4+}. In our case, the spray solution consisted of only $Ga(NO_3)_3$ having a 5 N purity, and none of the above-mentioned impurities was included intentionally. Furthermore, neither Zr nor Si were detected in our films by EDS analysis, although it is possible that they were present in amounts below the sensitivity limit of 0.1 at%. At any rate, it is possible that the broad blue–green emission is due to an inherent defect in the undoped Ga_2O_3 thin films.

Some researchers suggested that Ga_2O_3, which has not been doped intentionally, has a PL originating from the recombination of an electron on a donor formed by oxygen vacancies with a hole on an acceptor made up of either gallium vacancies or gallium–oxygen vacancy pairs (V_O, V_{Ga}) [9, 10, 21–23]. Because the thin films of Ga_2O_3 were prepared at much lower temperature than was used to produce powders and single crystals, it is possible that these films were oxygen deficient. Therefore, there could exist an appreciable amount of singly ionized oxygen vacancies, gallium vacancies or gallium–oxygen vacancy pairs (V_O, V_{Ga}) in sprayed Ga_2O_3 thin films. As a result, the emission shown in figure 6 could result from a rate-determining transfer of an electron from a donor (oxygen vacancy) to a hole trapped at an acceptor site (gallium vacancy or a gallium–oxygen vacancy pair). As indicated above, the broad emission band appears to consist of three Gaussian bands, and these may be associated with different transitions. Considering the band gap value of Ga_2O_3 in figure 4, those three emission peaks at 424 nm (2.92 eV), 497 nm (2.49 eV) and 526 nm (2.36 eV) could be attributed to: (a) recombination of electrons in shallow traps with holes in deep traps, (b) recombination of electrons in deep traps with holes in shallow traps, (c) recombination of electrons in deep traps with photo-excited or cathodo-excited holes in the valence band, (d) recombination of photo-excited or cathodo-excited electrons with holes in deep traps. These processes are shown in figure 7. In addition because the Ga_2O_3 film is polycrystalline, energy band bending will occur at grain boundaries raising the possibility that the depletion region may affect the emission process. Due to the complexity of the microscopic details, the exact mechanism(s) responsible for each emission peak is not clear. Furthermore, non-radiative recombination processes involving surface states, and defects from oxygen vacancies may be present and would lead to a decrease in the luminescence efficiency of the Ga_2O_3 phosphor.

Figure 8, which shows the effect of a variety of annealing ambients on the CL intensity of undoped Ga_2O_3 on glass,

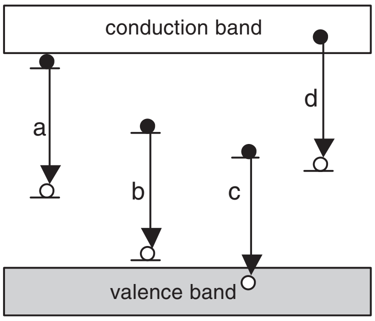

Figure 7. Schematic diagram of the energy band of Ga_2O_3. The carriers migrate through the solid and recombine via (a), (b), (c) and (d) paths.

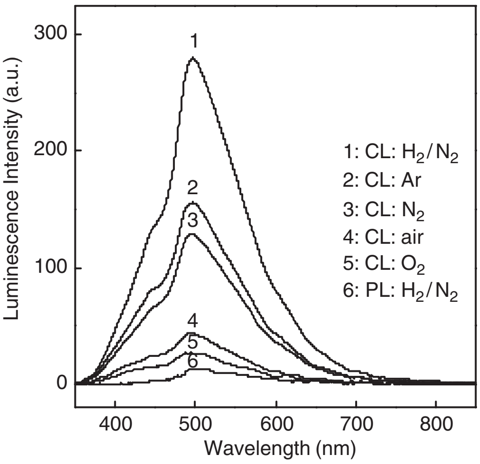

Figure 8. CL and PL spectra of thin films of Ga_2O_3 on glass in a variety of atmospheres. All annealing processes were employed at 600˚C for 1 h.

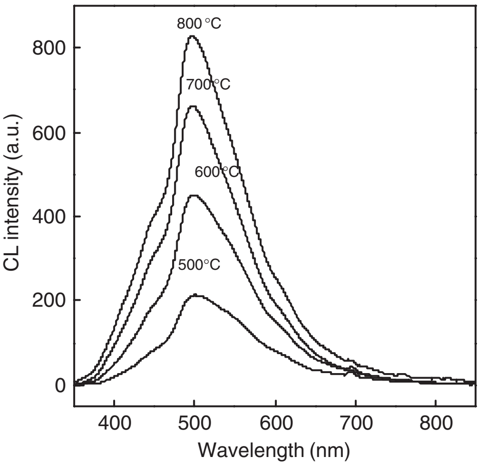

Figure 9. CL spectra of thin films of Ga_2O_3 for various annealing temperatures. Those samples were deposited on aluminosilicate substrates and annealed in forming gas for 1 h.

provides additional evidence for an oxygen vacancy model. All annealing processes employed 600˚C for 1 h. As can be seen, the intensity of CL emission band was affected strongly by the annealing ambient, though the line position and linewidth did not change. The annealing ambient changed from an oxidizing one (oxygen and air), through to an inert one (N_2 or Ar) and on to a reducing one (forming gas), corresponding to a change from oxygen-rich to oxygen-deficient Ga_2O_3 films. At the same time, the CL intensity grew for this sequence. This behaviour is consistent with the proposed oxygen vacancy model presented above and the one used to describe ZnO phosphors [24]. Thus, forming gas created more oxygen vacancies, and the CL intensity increased. On the other hand, the oxygen ambient decreased these vacancies and the CL intensity decreased. Also, the PL spectrum of the Ga_2O_3 film in figure 8 exhibits similar emission features and, therefore, may involve the same vacancies.

The dependence of the CL intensity on annealing temperature from 500˚C to 800˚C is shown in figure 9. These samples were deposited on aluminosilicate substrates and annealed in forming gas for 1 h. Also significant etching by forming gas due to the reduction of Ga_2O_3 to metallic Ga did not seem to be evident. The CL intensity was found generally to increase with increasing annealing temperature while emission peak position did not change. This increase may be due to two effects. First the crystallite size increases with higher annealing temperature. There are a number of papers that have demonstrated this effect. Second, the density of oxygen vacancies increases. This conclusion is consistent with earlier studies of reduced ZnO. Thus, as the annealing temperature of ZnO was increased, a correlation was found to occur between the increase in luminescence intensity and the increase in the intensity of an electron paramagnetic resonance (EPR) signal that was attributed to oxygen vacancies [24].

4. Conclusions

Thin films of undoped Ga_2O_3 and Ga_2O_3 doped with 1.0 at% Eu^{3+}, Tb^{3+} and Tm^{3+} were prepared by spray pyrolysis. Annealing in air or oxygen after deposition changed the morphology of Ga_2O_3 thin films and formed polycrystalline thin films with preferred peaks of (111) and (−310). Optical absorption of as-deposited Ga_2O_3 thin films at room temperature was altered by post-deposition annealing conditions. The CL spectra of $Ga_2O_3:Eu$ and $Ga_2O_3:Tb$ consisted of relatively sharp peaks that were characteristic of transitions between electronic energy levels of Eu^{3+} and Tb^{3+} ions. The CL of $Ga_2O_3:Tm$ mainly showed a broad band in the blue–green region, which was due in part to the Ga_2O_3 host. This broad emission from Ga_2O_3 host, consisting of three band peaks at 424 nm (2.92 eV), 497 nm (2.49 eV) and 526 nm (2.36 eV), was likely due to a recombination process that might include any of the four possible paths. The dependence of the CL intensity on the annealing atmosphere and temperature was consistent with a model that involved oxygen vacancies in the recombination.

Acknowledgments

This work was supported in part by a grant to M C from the Natural Sciences and Engineering Research Council of Canada.

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