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# Characterization of Photoluminescent $(Y_{1-x}Eu_x)_2O_3$ Thin-Films Prepared by Metallorganic Chemical Vapor Deposition

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## Abstract

Europium doped yttrium oxide,  $(Y_{1-x}Eu_x)_2O_3$ , thin-films were deposited on silicon and sapphire substrates by metallorganic chemical vapor deposition (MOCVD). The films were grown in a MOCVD chamber reacting yttrium and europium tris(2,2,6,6-tetramethyl-3,5-heptanedionates) precursors in an oxygen atmosphere at low pressures (5 Torr) and low substrate temperatures (500-700°C). The films deposited at 500°C were flat and composed of nanocrystalline regions of cubic  $Y_2O_3$ , grown in a textured [100] or [110] orientation to the substrate surface. Films deposited at 600°C developed from the flat, nanocrystalline morphology into a plate-like growth morphology oriented in the [111] with increasing deposition time. Monoclinic  $Y_2O_3:Eu^{3+}$  was observed in x-ray diffraction for deposition temperatures  $\geq 600^\circ C$  on both (111) Si and (001) sapphire substrates. This was also confirmed by the photoluminescent emission spectra.

## Introduction

Photo- and cathodoluminescent thin-films have potential application in emissive flat panel displays such as field emission and plasma panel displays. Field emission flat panel displays require thinner screens that operate under lower voltages, without sacrificing brightness or contrast. Thin-films, as opposed to the traditional discrete powder screens, offer the benefit of reduced light scattering, a reduction of material waste and the potential to fabricate smaller pixel sizes to enhance resolution. Europium doped yttrium oxide,  $(Y_{1-x}Eu_x)_2O_3$  ( $x=0.03-0.20$ ) or  $Y_2O_3:Eu^{3+}$ , is a well known photo- and cathodoluminescent material used for television screens and fluorescent lighting [1]. The fluorescent emission results from the  $5d \rightarrow 4f$  electronic transitions in the  $Eu^{3+}$  ion.

Figure 1 shows the energy level diagram for the free  $Eu^{3+}$  ion. Since the rare earth elements in a solid are shielded by the outer  $5s$  and  $5p$  electrons, the free ion scheme can be used to analyze the transitions occurring in an ionic crystal. Excitation of the  $Eu^{3+}$  ion results in the promotion of the electrons into the  $^5D_J$  manifold with emission occurring during relaxation to the  $^7F_J$  ground state manifold.

The luminescent properties of  $(Y_{1-x}Eu_x)_2O_3$  has mainly been studied as single crystals [2-6] at concentration levels of  $0.01 \leq x < 0.05$ .  $(Y_{1-x}Eu_x)_2O_3$  is an insulator, with a band gap energy of 5.6 eV and is strongly absorbing at energies with wavelengths  $< 250$  nm.  $Y_2O_3$  has a cubic space group,  $T_h^7$ , containing 8 yttrium sites of  $C_{3i}$  point symmetry and 24 sites of  $C_2$  point symmetry.

The ionic radii of  $Y^{3+}$  and  $Eu^{3+}$ , 0.092 nm and 0.098 nm, respectively, are similar and the  $Eu^{3+}$  ions populate the two different site symmetries with equal probability [6]. The emission spectrum is characterized by an intense, narrow feature at 611 nm arising from the  $^5D_0 \rightarrow ^7F_2$  transition from  $Eu^{3+}$  in the  $C_2$  site. Less intense features occurring in the 580-599 nm region arise from  $Eu^{3+}$  occupation of both the  $C_2$  and  $C_{3i}$  sites and involve the  $^5D_0 \rightarrow ^7F_1$  transitions. Figure 2 shows a typical photoluminescent (PL) excitation and emission spectra for powders of  $(Y_{1-x}Eu_x)_2O_3$ , with the transitions labeled.

It has been observed there are profound microstructural influences on the PL spectra of  $(Y_{1-x}Eu_x)_2O_3$  powders [7]. Small crystallite sizes, typically  $< 200$  nm show a weak fluorescence and increase in PL intensity with an increase in crystallite size. The increase in crystallite size is usually achieved by post-synthesis, high temperature annealing ( $> 1000^\circ C$ ). For very fine crystallite sizes, Eilers and Tissue [8] reported that both monoclinic  $Y_2O_3:Eu^{3+}$  and  $Eu_2O_3$  formed in nanocrystalline powders produced by gas condensation. Grytsiv et al. [9] found both cubic and monoclinic  $Y_2O_3$  in thin films prepared by reactive rf diode sputtering. The monoclinic phase of  $Y_2O_3$  is a high temperature phase that can be obtained in bulk by quenching under high pressure [10]. Nanocrystalline monoclinic  $Y_2O_3$  is thought to exist under ambient conditions due to the Gibbs-Thompson effect [11]. The fluorescence spectra of the 12 nm  $Y_2O_3:Eu^{3+}$  particles consist of a large feature at 625 nm and two smaller features at 615 and 619 nm, attributed to the  $^5D_0 \rightarrow ^7F_2$  transitions. Nanocrystalline  $Eu_2O_3$  shows a similar fluorescence spectrum to that of  $Y_2O_3:Eu^{3+}$ , except the feature at 615 nm is split into 2 features, centered around 615 nm. In later work, it was found that the solubility of  $Eu^{3+}$  in monoclinic  $Y_2O_3$  was lower than for cubic  $Y_2O_3$ : samples with  $\geq 0.7\%$   $Eu^{3+}$  were found to be composed of two phases, monoclinic  $Y_2O_3$  and  $Eu_2O_3$  [12]. Not all nanocrystalline  $Y_2O_3$  powders are monoclinic. For example, in combustion synthesized  $(Y_{1-x}Eu_x)_2O_3$  powders 14-26 nm in size, the monoclinic phase was not found [13]. It

appears that stabilization of the monoclinic phase is dependent on the processing technique, and is more likely to form at lower synthesis temperatures.

Thin-film ( $Y_{1-x}Eu_x$ )<sub>2</sub>O<sub>3</sub> has been deposited by low pressure metallorganic chemical vapor deposition (MOCVD) [14,15], spray pyrolysis [16] and pulsed laser ablation [17-19]. Independent of the deposition technique, the as-synthesized films were found to be weakly luminescent and required post-deposition annealing to increase the emission intensity. The increase in luminescence has been related to the crystallite size [20], similar to the effect found in powder samples. Films containing smaller crystallites have more grain boundaries, which are thought to be non-luminescent or even luminescence quenching regions [7]. It has been difficult to de-couple the thermal annealing effects, such as diffusion and lattice parameter changes, with the increase in grain size. In Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>, the C<sub>2</sub> sites (lower symmetry) have stronger transitions than the C<sub>3i</sub> sites (higher symmetry) [6]. It is possible that an entirely random distribution of Eu<sup>3+</sup> on the Y<sup>3+</sup> sites is not present in as-deposited thin-films, thereby altering the fluorescence spectrum. This could be especially true for high concentrations of Eu<sup>3+</sup>, in which Eu<sup>3+</sup>-Eu<sup>3+</sup> interactions could also modify the luminescent spectrum.

The purpose of this study was to identify and correlate the microstructural and luminescence properties of ( $Y_{1-x}Eu_x$ )<sub>2</sub>O<sub>3</sub> thin-films deposited by MOCVD as a function of deposition time and temperature. The influence of deposition parameters on the crystallite size and microstructural morphology has not been previously studied in this system. In addition, this research sought to quantify and separate crystallite size effects with other thermal effects on the resulting luminescent properties.

## Experimental Techniques

A schematic diagram of the stainless steel MOCVD system is depicted in Figure 3. The chamber is a cold-wall vertical reactor. The organometallic precursor is delivered to the reactor through a nozzle with a shower head. The shower head was located 10 cm above the hot stage. Sapphire substrates with the (001) face exposed, 2.54 cm in diameter and (111) Si pieces were placed on the hot stage. Stainless steel bubblers contained yttrium and europium tris(2,2,6,6,-tetramethyl-3,5-heptanedionates) precursors. The bubblers were heated to 146°C to sublime the organometallic species. Argon carrier gas passed through the heated bubblers to transport the vapor to the reaction chamber. The shower head, 3 cm in diameter, contained an array of 3 mm circular holes. Oxygen gas was used as the oxidant during the growth process. Oxygen flowed into the chamber through two inlets positioned at  $\pm 60^\circ$  to the substrates. During deposition the substrate temperature was maintained at temperatures between 500 and 700°C as monitored by a thermocouple. Mass flow controllers regulated the argon and oxygen flows. The total pressure inside the chamber was maintained with down stream control. Table I shows the deposition parameters.

After the deposition, the samples were allowed to cool to room temperature inside the chamber. Rutherford backscattering (RBS) was used to determine the europium concentration in the films. A chemical binding energy analysis to examine the sample purity was also performed at the surface using X-ray photoelectron spectroscopy (XPS) operated with an Al K $\alpha$  (1486.6 eV) X-ray source with a resolution of 1 at %. The crystallinity of the films were analyzed by X-ray diffraction (XRD) and observed by scanning electron microscopy (SEM). The crystallite size was measured by X-ray line broadening using Warren-Averbach analysis [21]. Small scratches were made on the films with a diamond stylus and the film thickness measured with a surface profilometer. Photoluminescence measurements were made with a CCD detector with an UV Hg excitation

source. A spot 2 mm in diameter was incident on the film and the emission spectra were collected in reflection mode with a 200  $\mu\text{m}$  fiber optic cable. Post-deposition processing consisted of annealing one sample deposited on sapphire at 600°C for 8 hours at 850°C for 24 and 108 hours.

## Results and Discussion

Figure 4 shows the XPS spectra for films grown at 700°C for 4 hours with two different europium  $\beta$ -diketonate carrier gas flow rates (10 and 20 sccm). The films show no detectable carbon peak present (270 eV). This indicates that the  $\beta$ -diketonates are excellent precursors for depositing high purity materials with a high degree of compositional control. The ease of stoichiometric control is attractive for compositions which require tightly controlled dopant concentrations. This processing flexibility is absent for deposition methods using single composition targets, such as physical vapor deposition techniques.

All films were luminescent in the as-deposited state, indicating the films were crystalline. The films were smooth and appeared continuous to the eye. Table II lists the thickness and europium concentration for a series of films deposited for 1, 2, 4 and 8 hours at 600°C. The growth rate was found to be 0.17  $\mu\text{m}/\text{hour}$ . However, the europium concentration ( $x$ ) decreased as the deposition time increased, which was not expected. West and Beeson have determined that  $x$  can be expressed by [14]:

$$x = \frac{C_{Eu} \exp \left[ \frac{-\Delta H_{Eu}}{RT_{Eu}} \right]}{C_{Eu} \exp \left[ \frac{-\Delta H_{Eu}}{RT_{Eu}} \right] + C_Y \exp \left[ \frac{-\Delta H_Y}{RT_Y} \right]} \quad (1)$$

where  $C_{Eu}$  and  $C_Y$  are constants,  $\Delta H_{Eu}$  and  $\Delta H_Y$  are the enthalpies of vaporization,  $R$  is the gas constant the  $T_{Eu}$  and  $T_Y$  are the reservoir temperatures of the precursors. It was found

experimentally that  $\Delta H_{Eu} = \Delta H_Y$  and that at 140°C,  $C_Y = 19C_{Eu}$ . With the reservoir temperatures held at 147°C, it is expected that  $x=0.05$ . A possible explanation for the high europium content found in all of the films coupled with the decrease in europium concentration with increasing deposition time could be related to the nucleation kinetics. Rutherford back scattering data also indicated that the europium concentration through the film thickness was not constant; a higher concentration existed near the substrate/film interface. It appears under these deposition conditions, nucleation of  $Y_2O_3$  may not be as rapid as  $Eu_2O_3$ .

XRD studies revealed a series of compositional and structural changes in the films deposited at different deposition temperatures on (100) sapphire substrates. Depositions for 6 hr at 500°C or 2 hours at 600°C were composed of cubic  $Y_2O_3$ , oriented in the [100] or [110] direction perpendicular to the substrate, as evidenced by the strong (400) and (440) peaks, as shown in Figure 5. This is supported by previous work that has shown MOCVD films grown on (001) sapphire substrates were oriented in the [100] but were randomly oriented when deposited on  $In_2O_3:Sn^{4+}$  coated glass substrates or polycrystalline  $Al_2O_3$  substrates [17]. In other work on MOCVD films of this composition deposited on polycrystalline  $Al_2O_3$  at 525°C, polycrystalline cubic  $(Y_{1-x}Eu_x)_2O_3$  was found [14].

A four hour deposition at 600°C showed peaks for cubic Y<sub>2</sub>O<sub>3</sub>. However, additional peaks are present that can be indexed to monoclinic Y<sub>2</sub>O<sub>3</sub>, as shown in Figure 5. Monoclinic Y<sub>2</sub>O<sub>3</sub> was also detected on films deposited on (111) Si. This is the first report of the observation of monoclinic (Y<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>O<sub>3</sub> in thin films. The cubic Y<sub>2</sub>O<sub>3</sub> pattern still reveals a strongly oriented growth in the [100] direction. This orientation becomes more defined than the 500°C depositions. After a four hr deposition at 700°C, the XRD pattern has narrower and more intense peaks with the most intense being the (222), indicating the films are textured in the [111]. Monoclinic Y<sub>2</sub>O<sub>3</sub> is still detected in the pattern, as shown in Figure 5, although the fraction is smaller compared to the 600°C sample. The XRD data is summarized in Table II. It appears that there is a minimum substrate temperature at which monoclinic Y<sub>2</sub>O<sub>3</sub> forms, and as the temperature increases, the volume fraction of monoclinic decreases as the amount of cubic increases.

These orientation results are in contrast to other work on pulsed laser deposited films on (100) Si and (111) diamond. The films were found to grow in a [111] direction at deposition temperatures ≤ 500°C while at higher deposition temperatures (≥ 700°C) there was a preferential [100] growth direction [18,19]. Reports indicate that the (111) surface is the low energy surface in Y<sub>2</sub>O<sub>3</sub>, thus growth of these surfaces would be preferred [19]. This was observed for the 700°C deposits. However, the initial orientation is along the [100], suggesting that the interface between the (001) sapphire and (100) Y<sub>2</sub>O<sub>3</sub> should be the low energy configuration.

SEM micrographs reveal different microstructural features in the films grown at different temperatures on Si. At 500°C, the films are cracked, as shown in Figure 6, apparently due to thermal expansion mismatch. The thermal stress in a thin film is given by [22]:

$$\sigma_f(T) = \frac{(\alpha_s - \alpha_f)(T - T_o)E_f}{1 - \nu_f} \quad (6)$$

where the subscripts f and s refer to the film and substrate, respectively. In equation (6), the film stress,  $\sigma_f$ , depends on the thermal expansion coefficient,  $\alpha$ , the measurement temperature,  $T$ , the deposition temperature,  $T_o$ , the elastic modulus,  $E$ , and Poisson's ratio,  $\nu$ . The thermal expansion coefficients for silicon and Y<sub>2</sub>O<sub>3</sub> are 4 and 8.1 × 10<sup>-6</sup>/°C, respectively and the modulus and Poisson's ratio for Y<sub>2</sub>O<sub>3</sub> are 151.7 GPa and 0.30, respectively [23]. The films would be in residual tension and the film stress is an order of magnitude larger than the flexural strength of Y<sub>2</sub>O<sub>3</sub> (123 MPa) [23]. The films deposited on sapphire do not show thermal cracking, as shown in Figure 7, since the thermal expansion coefficient of (001) sapphire is 9 × 10<sup>-6</sup>/°C. The film appearance is very similar to what was reported for MOCVD (Y<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>O<sub>3</sub> films deposited at 525°C [14].

Figure 8 shows a film deposited at 600°C for the two hours. The film is 0.40 μm thick. Cracking of the films is evident but the crystallites can be resolved with a size of ~150 nm. The film is similar to microstructures found on deposits on Si at 600°C and diamond by pulsed laser ablation [18,19]. Increasing the deposition time to four hours yields an entirely different microstructure, as shown in Figure 9. The film thickness has increased to 0.73 μm and the microstructure consists of an unusual platelet-type growth. This was not previously observed in films of this composition. Despite the thermal mismatch, the films are not cracked, which may be due to the discontinuity of the grains in the microstructure. Increasing the deposition temperature to 700°C for 4 hours yields a similar but coarser microstructure as for the 600°C deposition, as shown in Figure 10. However these films are strongly oriented in the [111]. The microstructural development appears to be the initial nucleation of cubic Y<sub>2</sub>O<sub>3</sub> oriented in the [100] or [110], due to interfacial energy constraints



between sapphire and  $\text{Y}_2\text{O}_3$ . Higher deposition temperatures promotes growth of the low energy (111) surface of cubic  $\text{Y}_2\text{O}_3$  along with the nucleation of monoclinic  $\text{Y}_2\text{O}_3$ . It is possible that the presence of monoclinic  $\text{Y}_2\text{O}_3$  affects the growth and morphology of the cubic  $\text{Y}_2\text{O}_3$ . The platelet-type growth is also observed on sapphire substrates, indicating that stress relief alone does not promote this type of growth.

Photoluminescent measurements taken on films grown on sapphire reveal that increasing the substrate temperature increases the intensity of the emission spectrum, as shown in Figure 11.

$\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  is cubic and orientation effects are not expected to influence the PL spectra. The features for all samples are broad (as compared to Figure 2) indicating a large degree of disorder around the  $\text{Eu}^{3+}$  ion. There is a larger increase in the emission intensity on increasing the substrate temperature from 500 to 600°C as compared to increasing the temperature from 600 to 700°C.

Since the strong 611 nm features is a very good indicator of the presence of cubic  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ , this phase is present in all of the films. The large feature at 628 nm has been attributed to monoclinic  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  [8,12]. Although monoclinic  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  was not detected by XRD in the 500°C deposits, a small amount of this phase must be present in these films since spectroscopic techniques are more sensitive in detecting small amounts of materials than XRD. Increasing the deposition temperature increases the intensity of the 611 nm features relative to the 628 nm feature, indicating that the volume fraction of cubic  $\text{Y}_2\text{O}_3$  is increasing. The amounts of monoclinic and cubic cannot be determined from these measurements. The emission intensity increase can be attributed to both grain growth (minimizing grain boundary area) and a reduction of disorder around the  $\text{Eu}^{3+}$  in the lattice.

Because of the presence of the 611 nm feature in the samples, it is not unreasonable to account for the feature center around 628 nm to be an effect of a high  $\text{Eu}^{3+}$  concentration, especially for the low temperature depositions. The transitions shown in Figure 1 can be used in solids where a low concentration of  $\text{Eu}^{3+}$  is present. The influence of  $\text{Eu}^{3+}$ - $\text{Eu}^{3+}$  interaction and subsequent affect on the luminescent spectrum is not known.

To analyze the influence of crystallite size on luminescent properties, a film deposited at 600°C for 8 hours on sapphire was post-annealed at 850°C for 24 or 108 hours to promote crystallite growth. Figure 12 shows an increase of the XRD peak intensity is induced with the longer annealing treatments. Sharper peaks are also observed along with a slight shift in peak location. The sharpening of the peaks indicates an increase in crystallite size and the shift in the peak location indicates a decrease in the lattice parameter. Photoluminescent measurements taken on the same films as shown in Figure 12 are presented in Figure 13. The PL intensity increases along with an increase in crystallite size. Table III summarizes the structural and luminescent data taken on the as-deposited and annealed samples. The area under the PL spectra was integrated between 550-650 nm to obtain the integrated intensity. Comparing the as-deposited sample with the 108 hour annealed sample, the crystallite size increased by 26%, which is closely correlated with the increase in PL integrated intensity (20%). The change in lattice parameter was only 0.12%, indicating that this had less of an influence on the PL emission behavior than the change in crystallite size. Thermal effects (diffusion, sublimation of volatile species, grain growth) are known to improve luminescent emission intensity in powders [24] and films [14,17]. However, these results show that the increased crystallite size, whether induced by an increase in temperature or an increase in annealing time, is the dominant mechanism for improved PL emission intensity. This can be attributed to a reduction in the grain boundary area, a region with a high density of defects that could quench luminescence emission.

## Conclusions

Thin-films of  $(Y_{1-x}Eu_x)_2O_3$  were deposited by low-pressure metallorganic vapor deposition with Y- and Eu-tris(2,2,6,6-tetramethyl-3,5-heptanedionates) precursors on (001) sapphire and (111) Si substrates. The as-deposited films were crystalline and luminescent and carbon contamination was not detected. The growth rate was found to be  $0.17 \mu\text{m/hr}$  at  $600^\circ\text{C}$  with the yttrium and europium reservoirs at  $147^\circ\text{C}$  and carrier gas flow rates of 100 and 10 sccm, respectively. The films deposited at  $500^\circ\text{C}$  were flat and were composed of nanocrystalline regions which showed thermal cracking on Si substrates but not on sapphire substrates. These films were composed of cubic  $Y_2O_3$ , grown in a textured [100] or [110] orientation to the substrate surface. Films deposited at  $600^\circ\text{C}$  developed from the flat, nanocrystalline morphology (2 hours) into a plate-like growth morphology oriented in the [111] with increasing deposition time (4 hours). Monoclinic  $Y_2O_3:Eu^{3+}$  was observed for deposition temperatures  $\geq 600^\circ\text{C}$  on both (111) Si and (001) sapphire substrates, which also correlated with the photoluminescent emission spectra. An increase of the deposition temperature increased the photoluminescent intensity which was attributed to a reduction in grain boundary area and a decrease in ionic disorder around the  $Eu^{3+}$ . Post-deposition annealing at a fixed temperature increased the crystallite size and decreased the lattice parameter. The former was more effective in increasing the PL intensity than the latter.

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## References

1. K. A. Franz, W. G. Kehr, A. Siggel, J. Wiczoreck, in Ullmann's Encyclopedia of Industrial Chemistry, eds. B. Elvers, S. Hawkins, and G. Schulz, **A15**, VCH Publishers, Weinheim, Germany 1985.
2. K.A. Wickersheim and R.A. Lefever, "Luminescent Behavior of the Rare Earths in Yttrium Oxide and Related Hosts," *J. Electrochem. Soc.*, **111** [1] 47-51 (1964).
3. N.C. Chang and J.B. Gruber, "Spectra and Energy Levels of  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_3$ ," *J. Chem. Phys.*, **41** [10] 3227-3234 (1964).
4. M.J. Sellars, R.S. Meltzer, P.T.H. Fisk and N.B. Manson, "Time-Resolved Ultranarrow Optical Hole Burning of a Crystalline Solid:  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ ," *J. Opt. Soc. Am. B*, **11**[8] 1468-1473 (1994).
5. N.C. Chang, "Fluorescence and Stimulated Emission from Trivalent Europium in Yttrium Oxide," *J. Appl. Phys.*, **34** [12] 3500-3504 (1963).
6. J. Heber, K.H. Hellwege, U. Köbler and H. Murmann, "Energy Levels and Interaction between  $\text{Eu}^{3+}$ -ions at Lattice Sites of Symmetry  $\text{C}_2$  and Symmetry  $\text{C}_{3i}$  in  $\text{Y}_2\text{O}_3$ ," *Z. Physik*, **237** 189-204 (1970).
7. L.E. Shea, J. McKittrick and M.L.F. Phillips, "Predicting and Modeling the Low-Voltage Cathodoluminescent Efficiency of Oxide Phosphors," *J. Electrochem. Soc.*, accepted.
8. H. Eilers and B.M. Tissue, "Laser Spectroscopy of Nanocrystalline  $\text{Eu}_2\text{O}_3$  and  $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$ ," *Chem. Phys. Lett.*, **251** 74-78 (1996).
9. M. Ya. Grytsiv, V.D. Bondar and S.I. Chykhrii, "Structure of Yttria Thin Films Prepared by Reactive RF Diode Sputtering," *Inorg. Mat.*, **32** [11] 1202-1204 (1996).
10. H.R. Hoekstra and K.A. Gingerich, "High-Pressure B-Type Polymorphs of Some Rare-Earth Sesquioxides," *Science*, **146** [3647] 1163-64 (1964).
11. G. Skandan, C.M. Foster, H. Frase, M.N. Ali, J.C. Parker and H. Hahn, "Phase Characterization and Stabilization Due to Grain Size Effects of Nanostructured  $\text{Y}_2\text{O}_3$ ," *Nanostruc. Mat.*, **1** 313-322 (1992).
12. B. Bihari, H. Eilers, B.M. Tissue, "Spectra and Dynamics of Monoclinic  $\text{Eu}_2\text{O}_3$  and  $\text{Eu}^{3+}:\text{Y}_2\text{O}_3$  Nanocrystals," *J. Lumin.*, **75** 1-10 (1997).
13. M. Kottaisamy, D. Jeyakumar, R. Jagannathan and M. Mohan Rao, "Yttrium Oxide: $\text{Eu}^{3+}$  Red Phosphor by Self-Propagating High Temperature Synthesis," *Mater. Res. Bull.*, **31** [8] 1013-1020 (1996).
14. G.A. West and K.W. Beeson, "Low-Pressure Metalorganic Chemical Vapor Deposition of Photoluminescent Eu-doped  $\text{Y}_2\text{O}_3$  Films," *J. Mater. Res.*, **5** [7] 1573-1580 (1990).
15. J.P. Dismukes, J. Kane, B. Binggeli and H.P. Schweizer, "Chemical Vapor Deposition of Cathodoluminescent Phosphor Layers," in Chemical Vapor Deposition: Fourth International Conference, eds. G.F. Wakefield and J.M. Blocher, The Electrochemical Society, Princeton, NJ, 1973.
16. H.P. Maruska, T. Parodos, N.M. Kalkhouraud and W.D. Halverson, "Challenges for Flat Panel Display Phosphors," *Mat. Res. Soc. Symp. Proc.*, **345** 269-280 (1994).
17. G. A. Hirata, J. McKittrick, M. Avalos-Borja, J. M. Siqueiros and D. Devlin, "Physical Properties of  $\text{Y}_2\text{O}_3:\text{Eu}$  Luminescent Films Grown by MOCVD and Laser Ablation," *Appl. Surf. Sci.*, **113/114** 509-514 (1997).
18. K.G. Cho, D. Kumar, D.G. Lee, S.L. Jones, P.H. Holloway and R.K. Singh, "Improved Luminescence Properties of Pulsed Laser Deposited  $\text{Eu}:\text{Y}_2\text{O}_3$  Thin Films on Diamond Coated Silicon Substrates," *Appl. Phys. Lett.*, **71** [23] 3335-3337 (1997).

19. S.L. Jones, D. Kumar, R.K. Singh and P.H. Holloway, "Luminescence of Pulsed Laser Deposited Eu Doped Yttrium Oxide Films," *Appl. Phys. Lett.*, **71** [3] 404-406 (1997).
20. G.A. Hirata, J. McKittrick, J. Yi, S.G. Pattillo, K.V. Salazar and M. Trkula, "Microstructural and Photoluminescence Studies on Europium Doped Yttrium Oxide Films Synthesized by Metallorganic Vapor Deposition," *Mat. Res. Soc. Symp. Proc.*, accepted.
21. D. Balzar, "Profile Fitting of X-ray Diffraction Lines and Fourier Analysis of Broadening," *J. Appl. Cryst.*, **25**, 559-570 (1992).
22. M. Ohring, The Materials Science of Thin Films, Academic Press, Inc., San Diego, CA, 1992.
23. Engineering Property Data on Selected Ceramics, Vol. I, Single Oxides, MCIC Report-HB-07, Metals and Ceramics Information Center, Battelle, Columbus, Ohio, 1981.
24. L.E. Shea, J. McKittrick, O.A. Lopez, E. Sluzky, "Synthesis of Red-Emitting, Small Particle Size Luminescent Oxides Using an Optimized Combustion Process," *J. Am. Ceram. Soc.*, **79** [12] 3257-65 (1996).
25. L. Ozawa, Cathodoluminescence, Theory and Application, VCH Publishers, Weinheim, Germany, 1990.

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substrate	sapphire or Si
substrate temperature	500-700°C
carrier gas	argon
metallorganic precursors	Y- or Eu-tris (2,2,6,6-tetramethyl-3,5-heptanedionate)
Y carrier gas flow rate	100 sccm
Eu carrier gas flow rate	10 sccm
Y reservoir temperature	146°C
Eu reservoir temperature	146°C
oxygen gas flow rate	100 sccm
chamber pressure	5 Torr
deposition time	1 - 8 hours

**Table I** MOCVD deposition parameters.

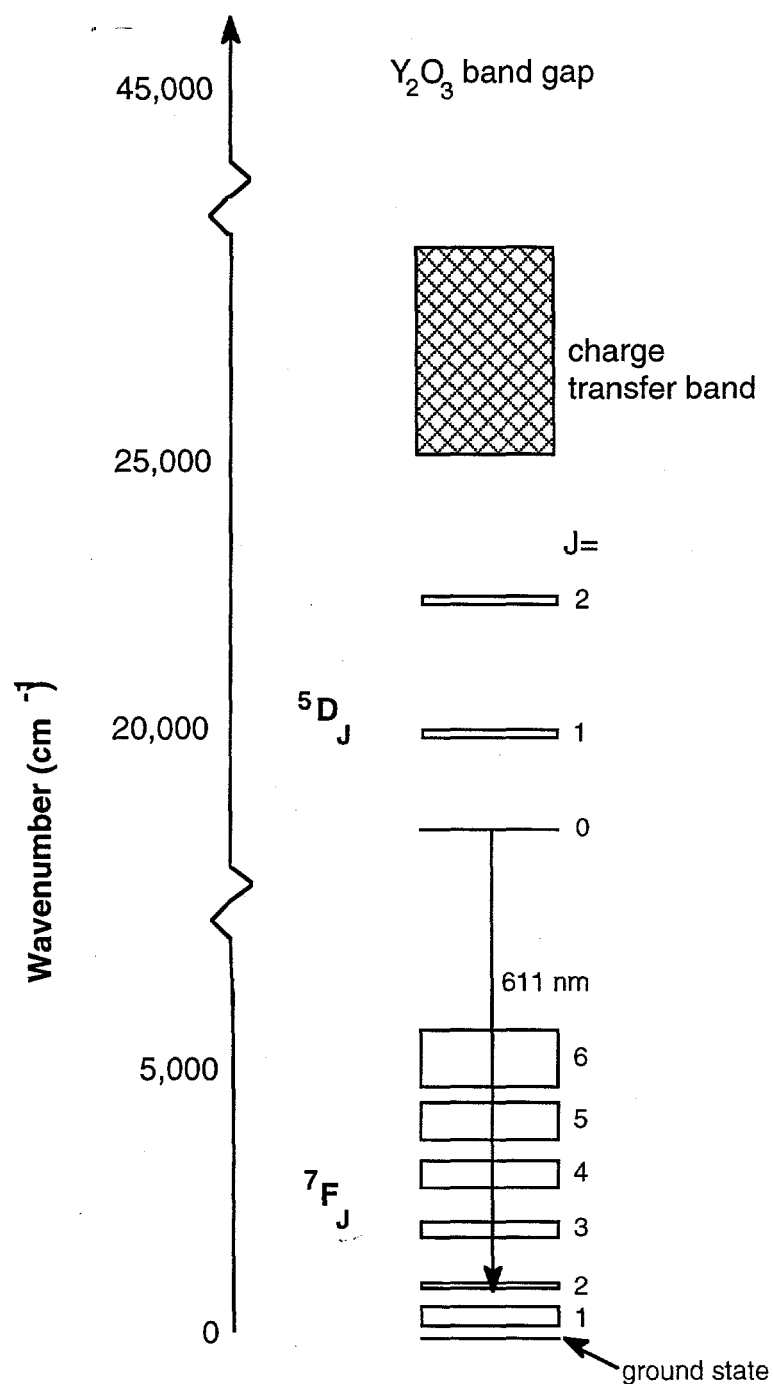
substrate temperature (°C)	Eu flow (sccm)	time (hours)	thickness (μm)	europium concentration	phases present (on Si substrates)
500	10	6	1.38		c-Y <sub>2</sub> O <sub>3</sub> [100] and [110]
600	10	1	0.03-0.10	0.31	*
600	10	2	0.40	0.29	c-Y <sub>2</sub> O <sub>3</sub> [100] and [110]
600	10	4	0.73	0.18	c+m-Y <sub>2</sub> O <sub>3</sub> [100]
700	10	4	1.51		c+m-Y <sub>2</sub> O <sub>3</sub> [111]

\* signal too weak

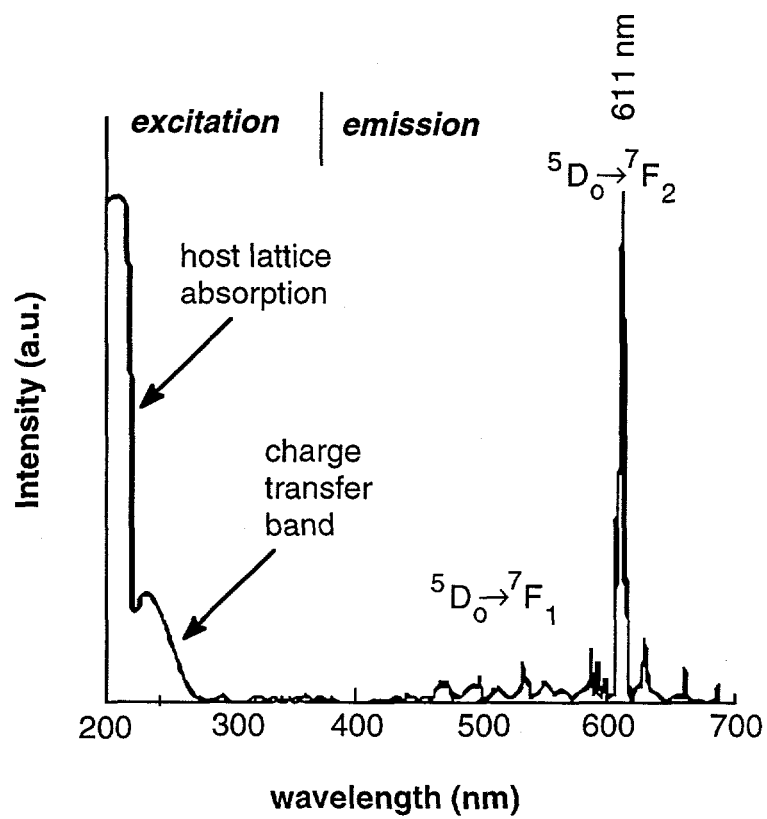
**Table II.** Film thickness, x in (Y<sub>1-x</sub>Eu<sub>x</sub>)<sub>2</sub>O<sub>3</sub> and phases present.

condition	lattice parameter (nm)	crystallite size (nm)	normalized PL integrated intensity
as-synthesized	1.0632	17	1.0
850°C, 24 hours	1.0624	20	1.1
850°C, 108 hours	1.0619	23	1.2

**Table III** Summary of data taken on Y<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> films on sapphire deposited for eight hours at 600°C and then heat treated to 850°C for 24 or 108 hours.

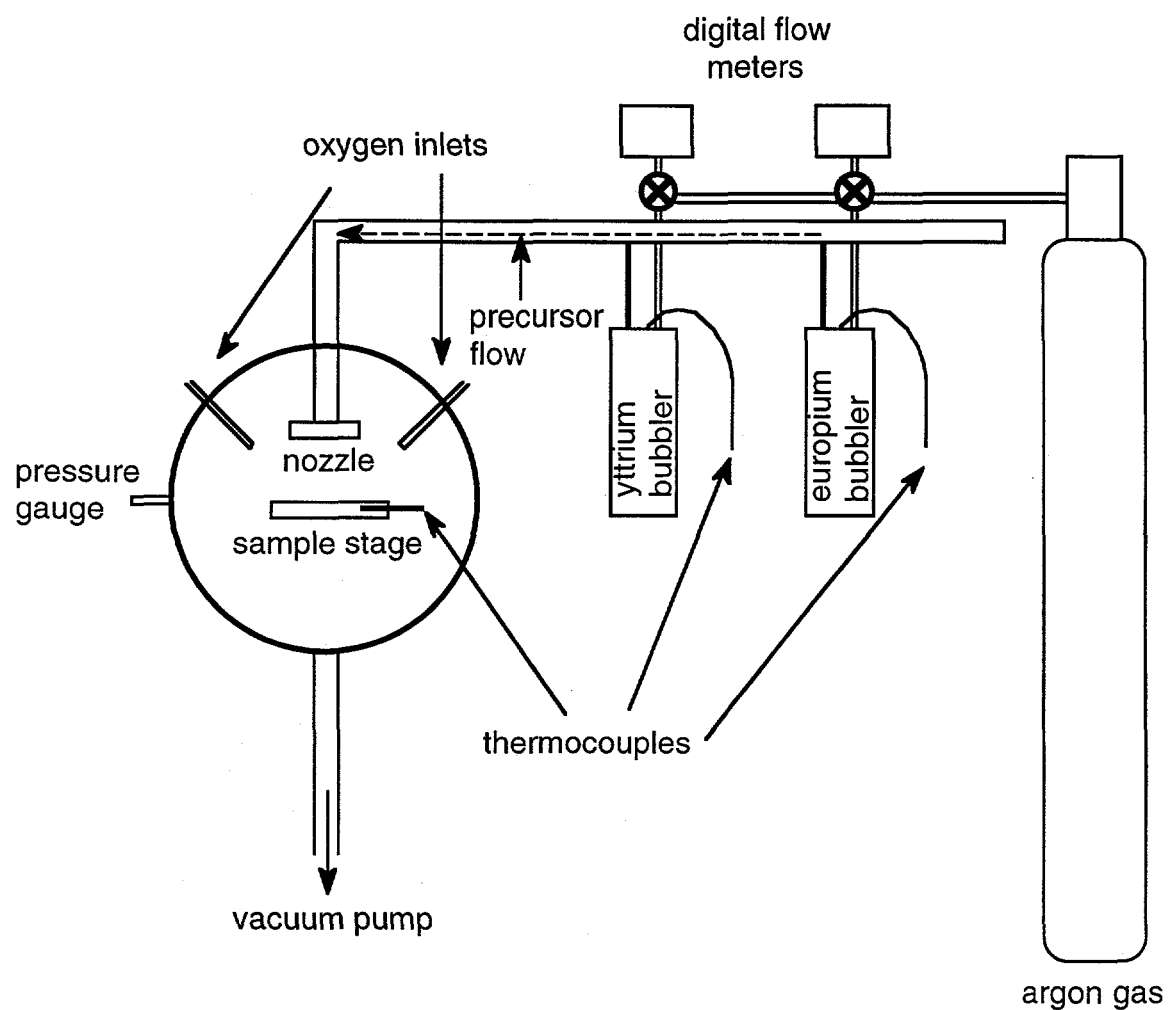


**Figure 1** Partial energy level diagram for  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_3$ . The strong transition causing the 611 nm feature in the fluorescence spectra is shown. The charge transfer is the lowest level absorption band in this system with the band gap absorption occurring at a higher energy level. Adapted from [5].

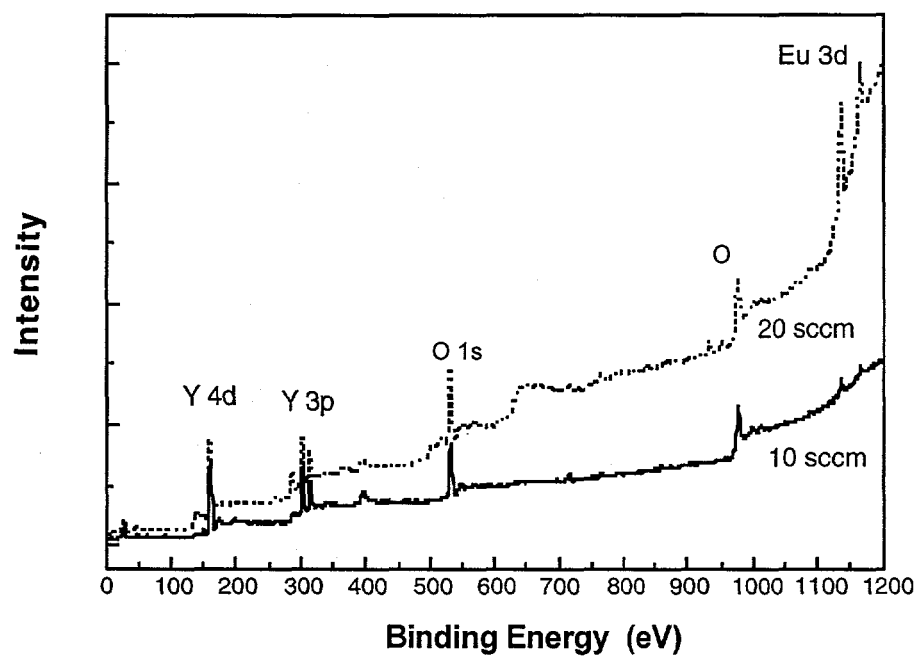


**Figure 2** Typical fluorescence spectrum for  $(Y_{1-x}Eu_x)_2O_3$  powders. Adapted from [26].

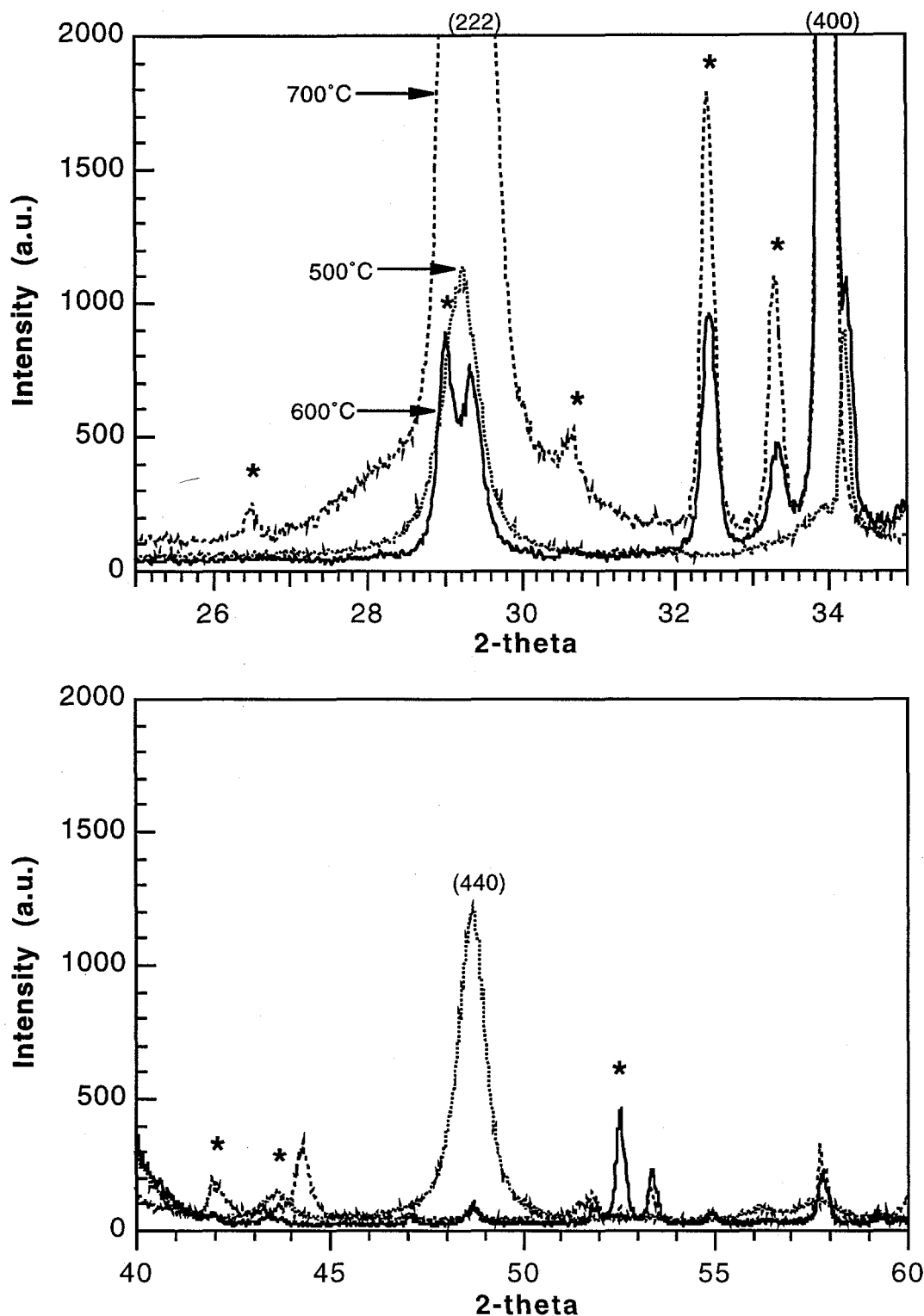




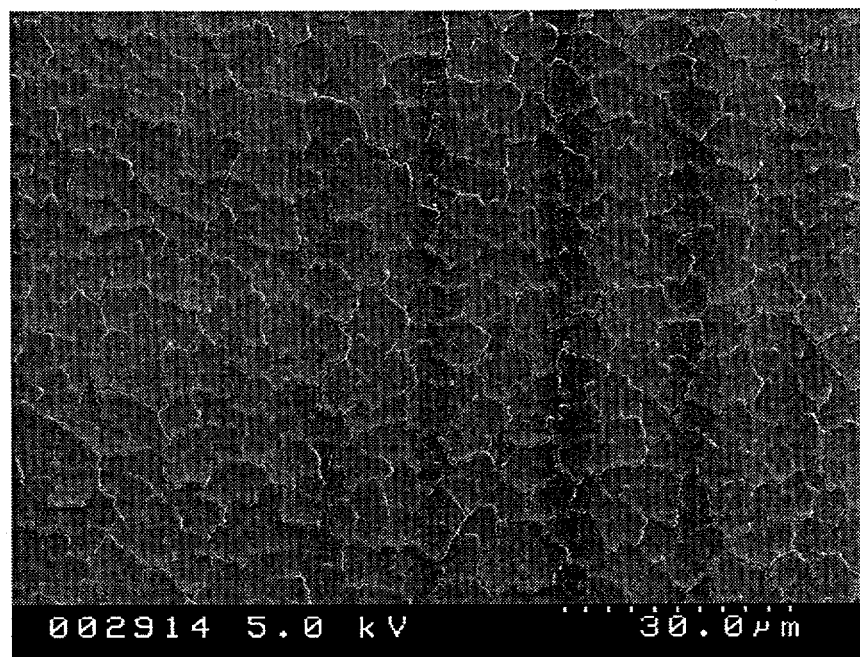
**Figure 3** Schematic diagram of the MOCVD chamber.



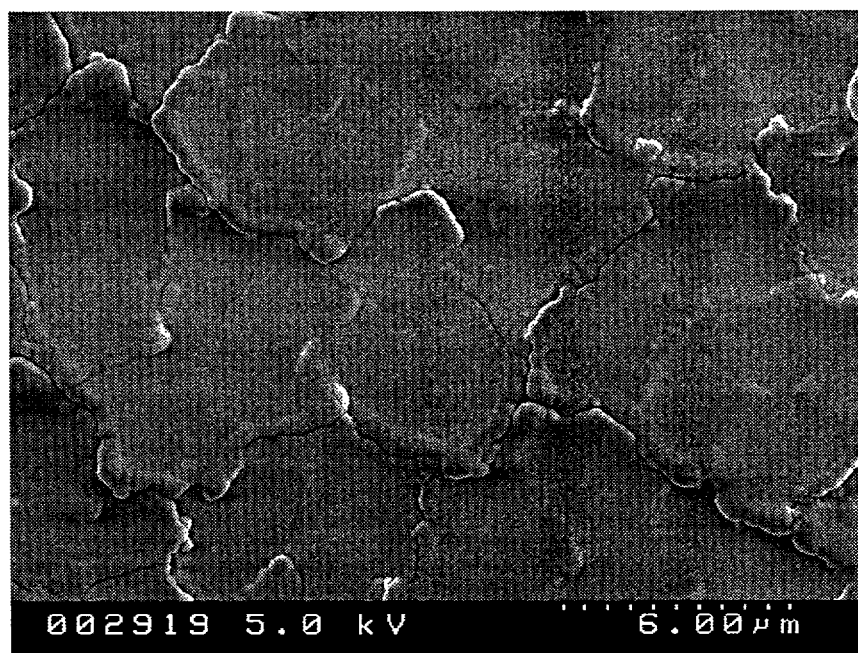
**Figure 4** XPS spectra for films grown with a Eu  $\beta$ -diketonate flow rate of (a) 10 sccm and (b) 20 sccm.



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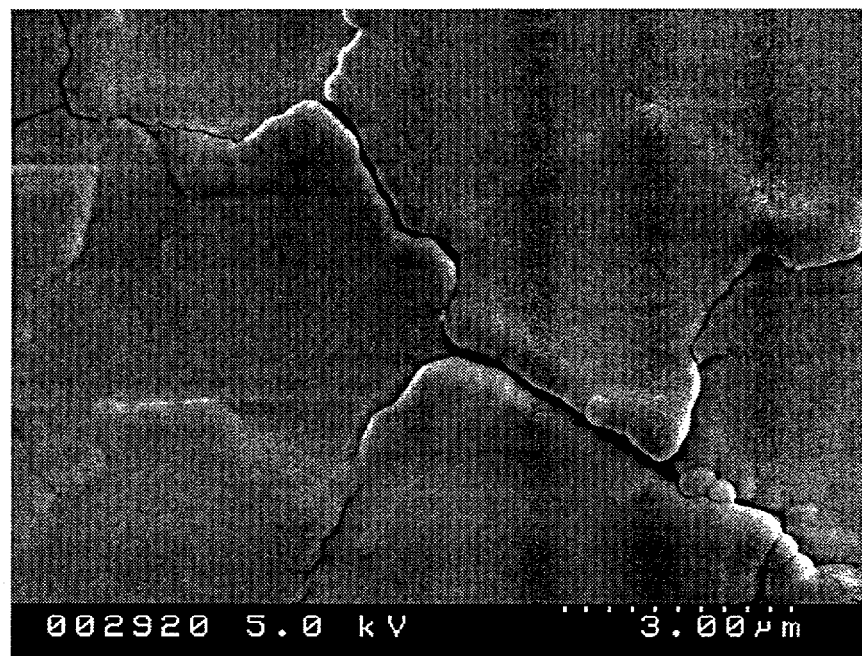


(a)



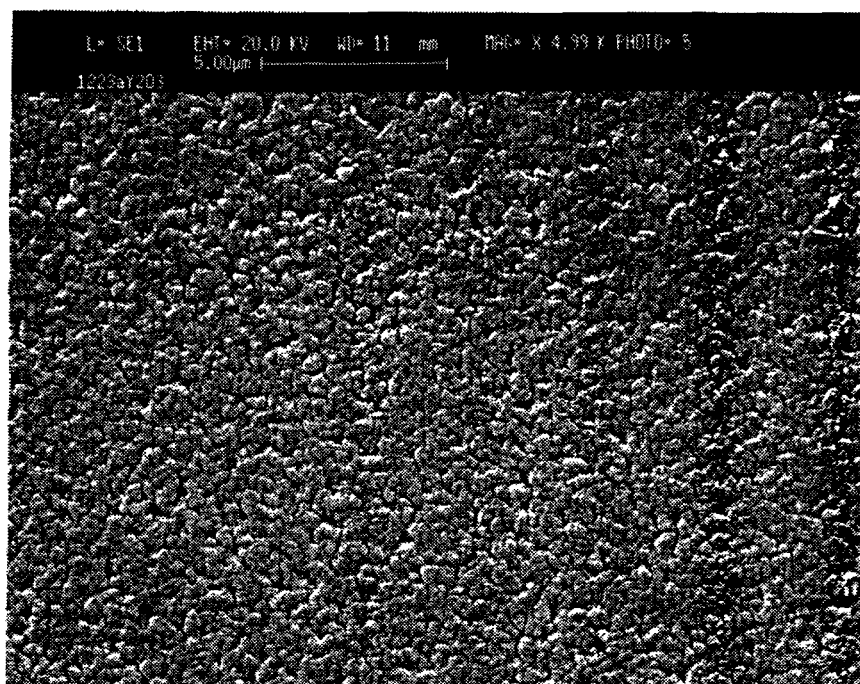
(b)

**Figure 6** SEM micrographs of the films deposited at 500°C for six hours, (a) 1000X, (b) 5000X and (c) 10,000X.

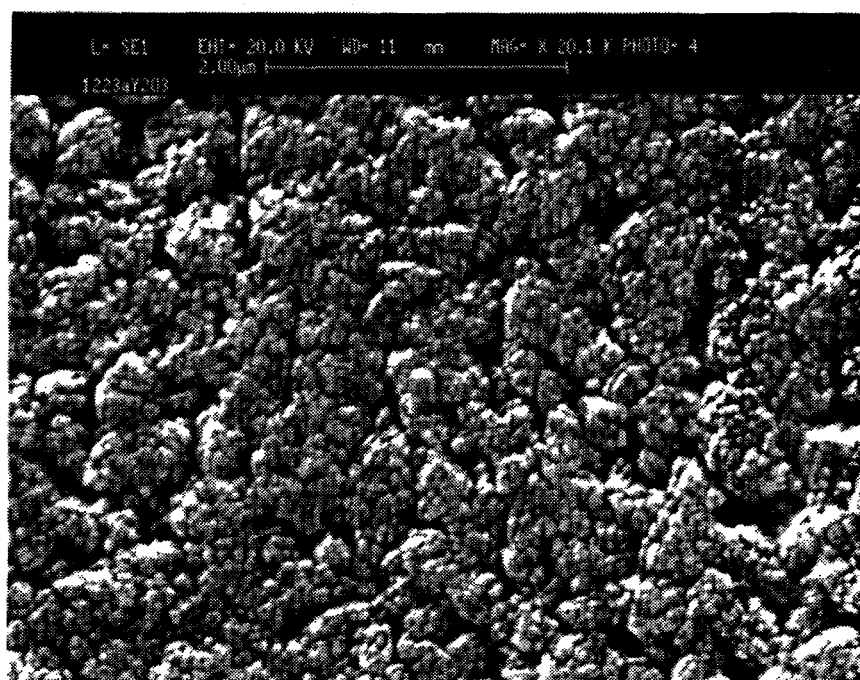


(c)

**Figure 6** SEM micrographs of the films deposited at 500°C for six hours, (a) 1000X, (b) 5000X and (c) 10,000X.

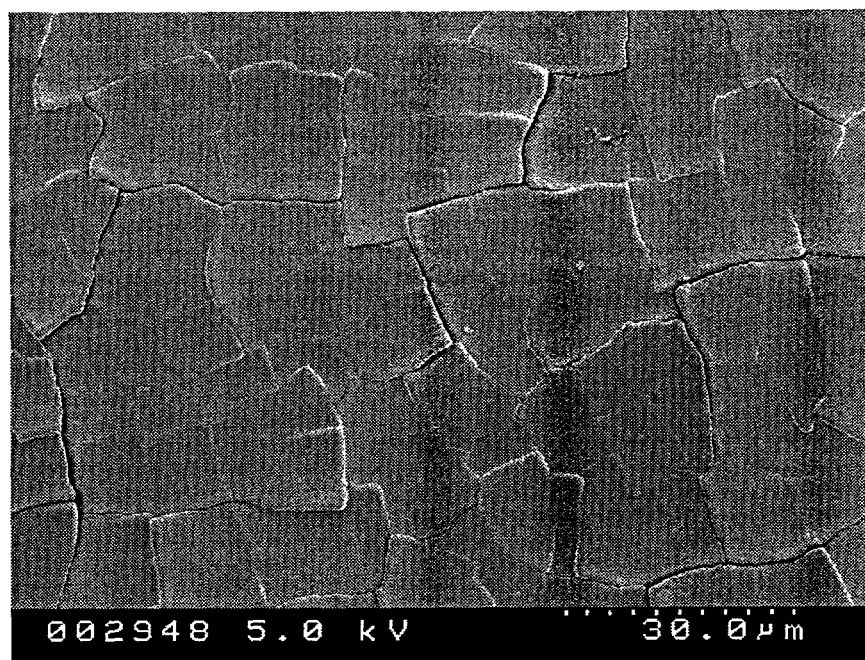


(a)

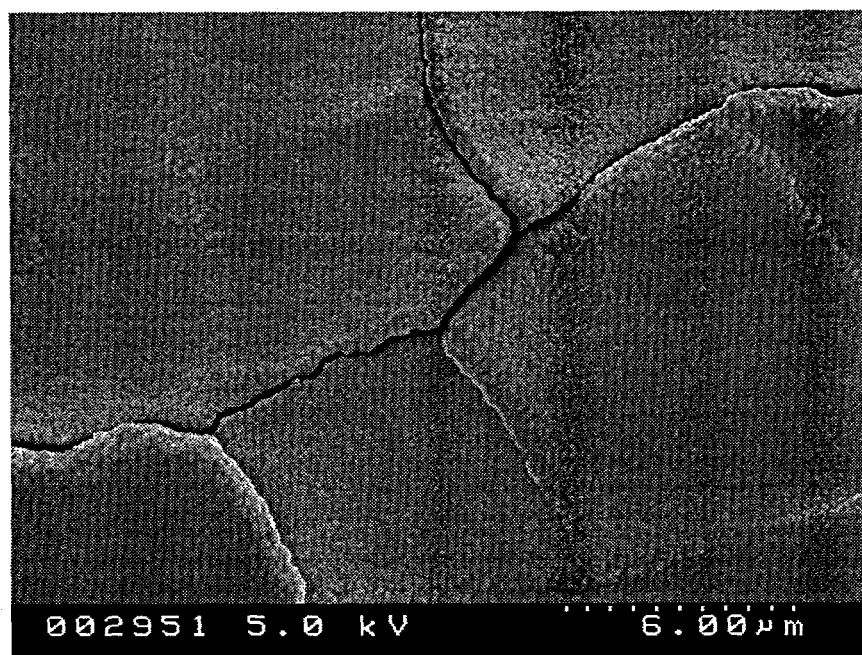


(b)

**Figure 7** SEM micrographs of films deposited for six hours at 500°C on sapphire (a) 4000X and (b) 20,000X.

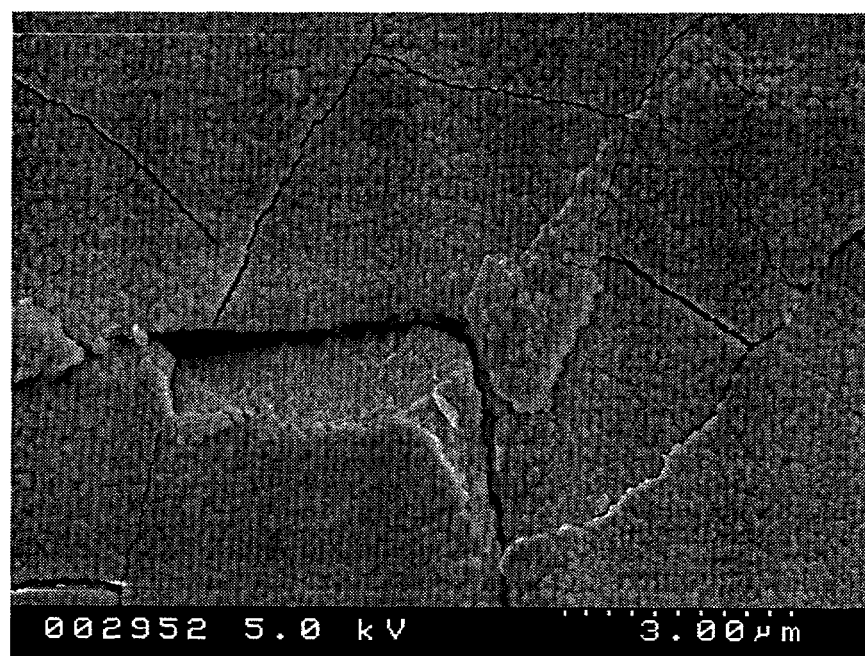


(a)



(b)

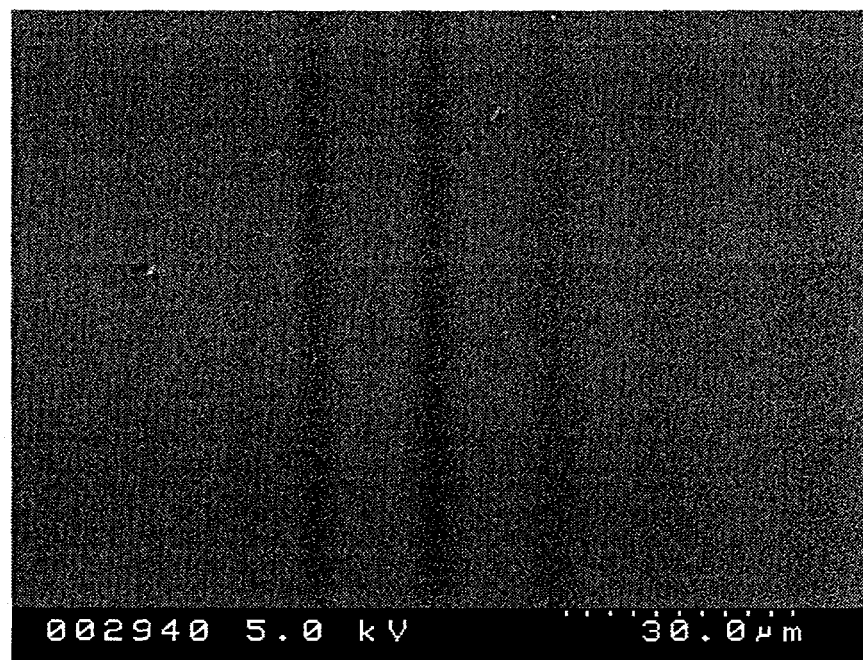
**Figure 8** SEM micrographs of the films deposited at 600°C for two hours, (a) 1000X, (b) 5000X and (c) 10,000X.



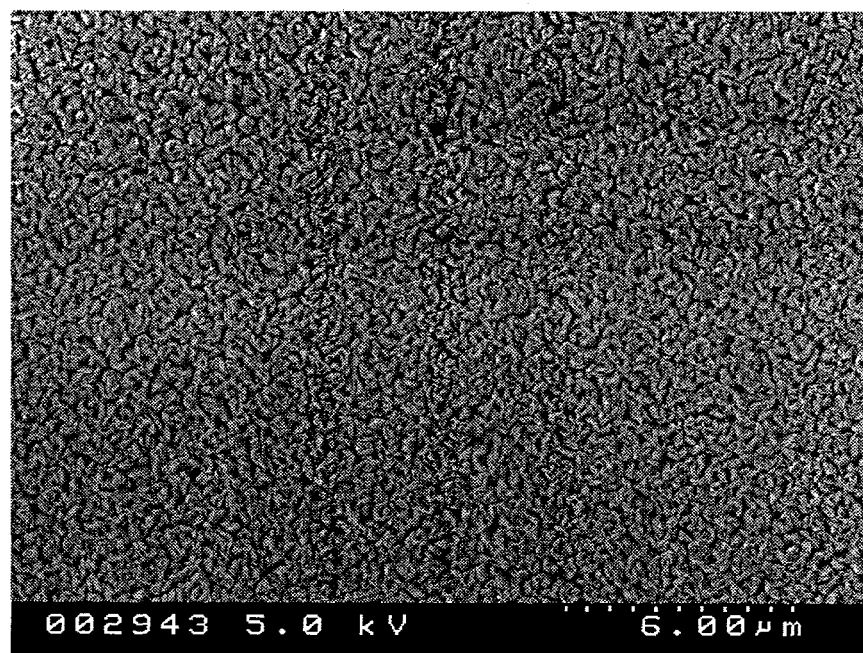
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**Figure 8** SEM micrographs of the films deposited at 600°C for two hours, (a) 1000X, (b) 5000X and (c) 10,000X.



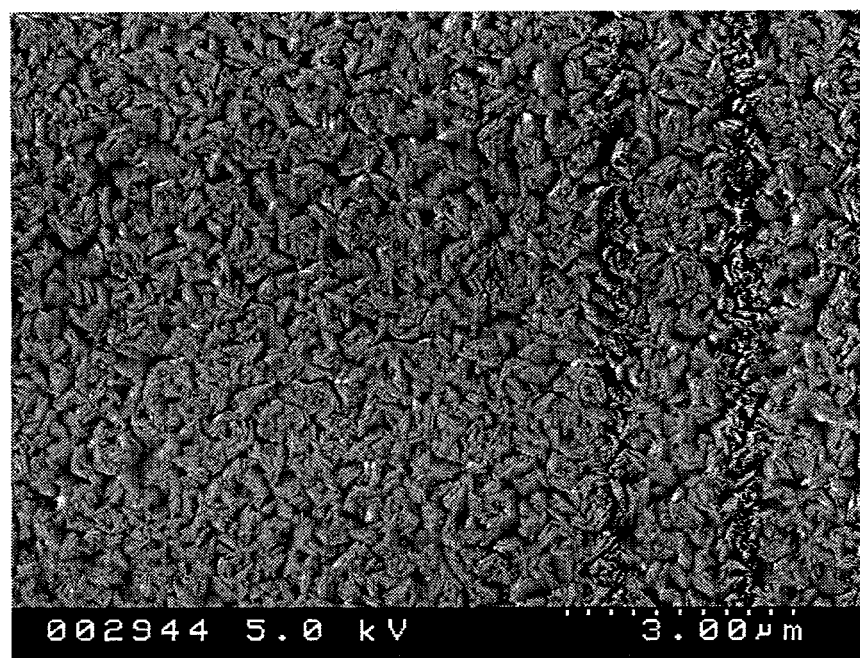


(a)



(b)

**Figure 9** SEM micrographs of the films deposited at 600°C for four hours, (a) 1000X, (b) 5000X and (c) 10,000X.

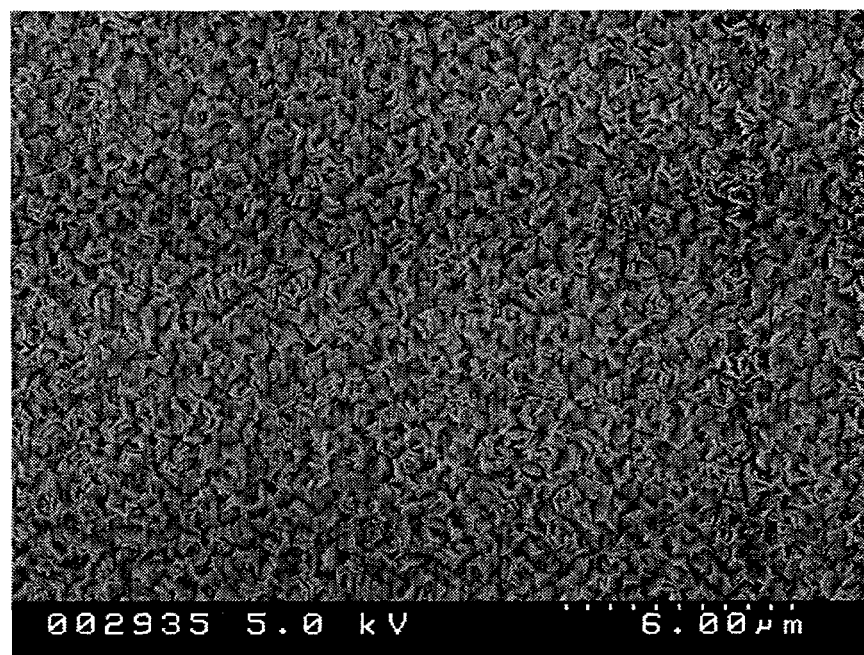


(c)

**Figure 9** SEM micrographs of the films deposited at 600°C for four hours, (a) 1000X, (b) 5000X and (c) 10,000X.

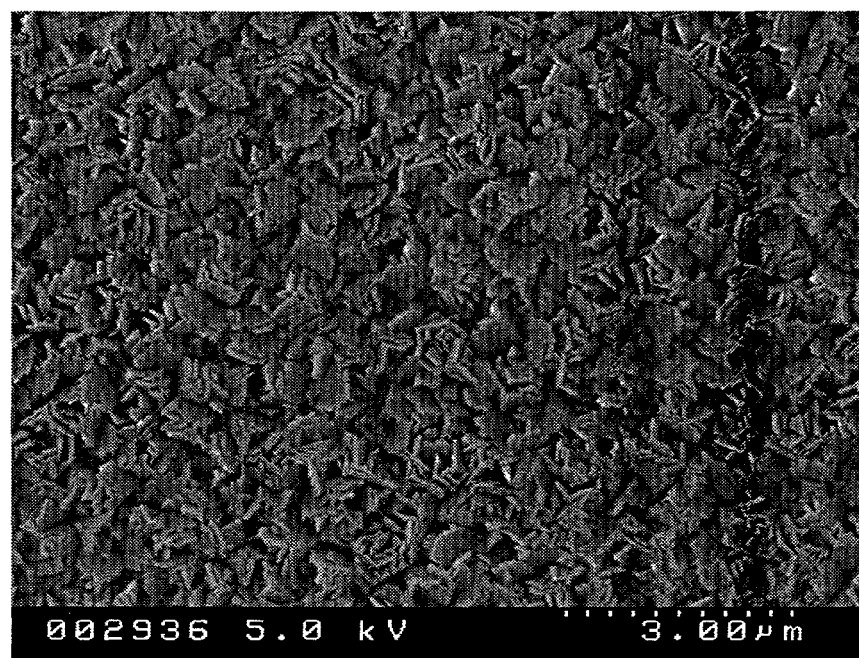


(a)



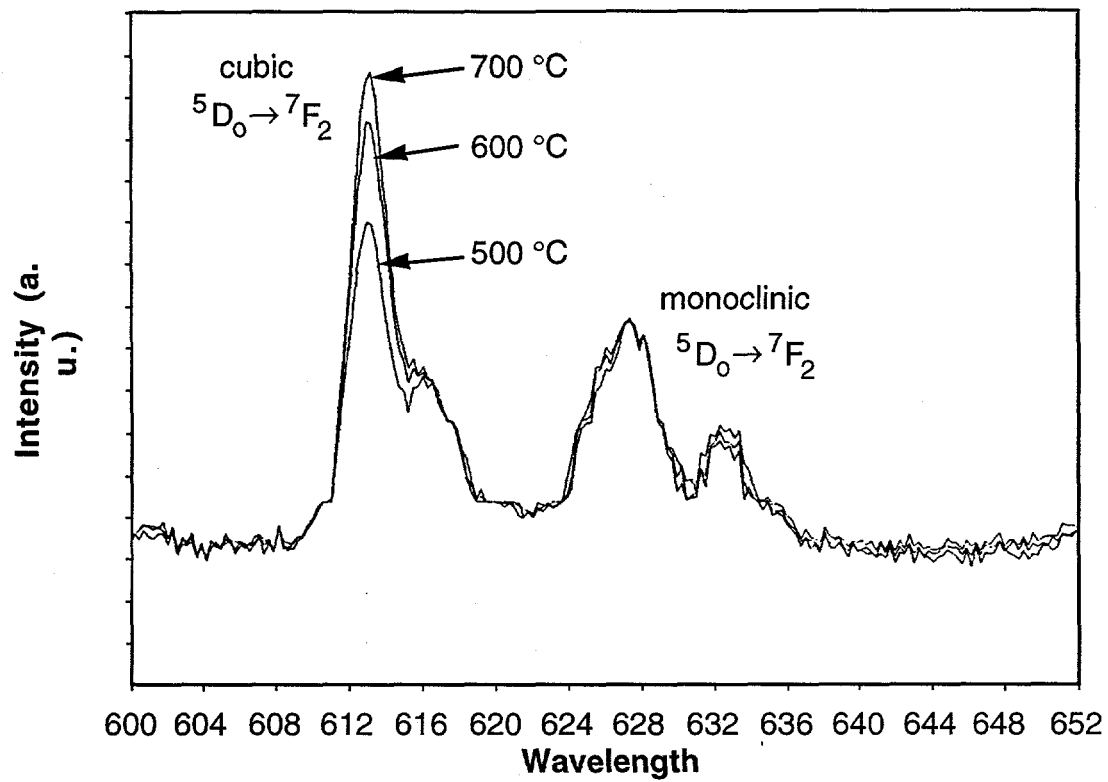
(b)

**Figure 10** SEM micrographs of the films deposited at 700°C for four hours, (a) 1000X, (b) 5000X and (c) 10,000X.

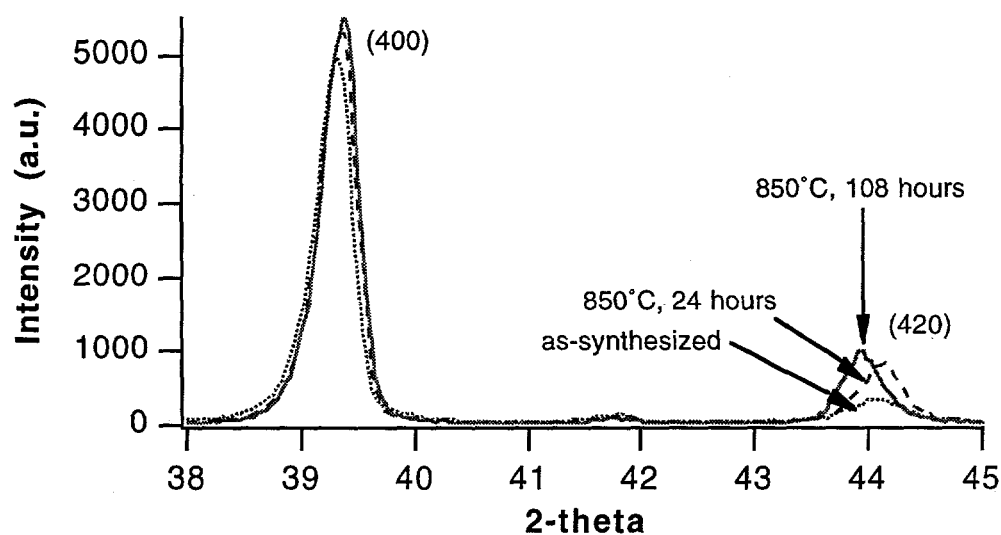


(c)

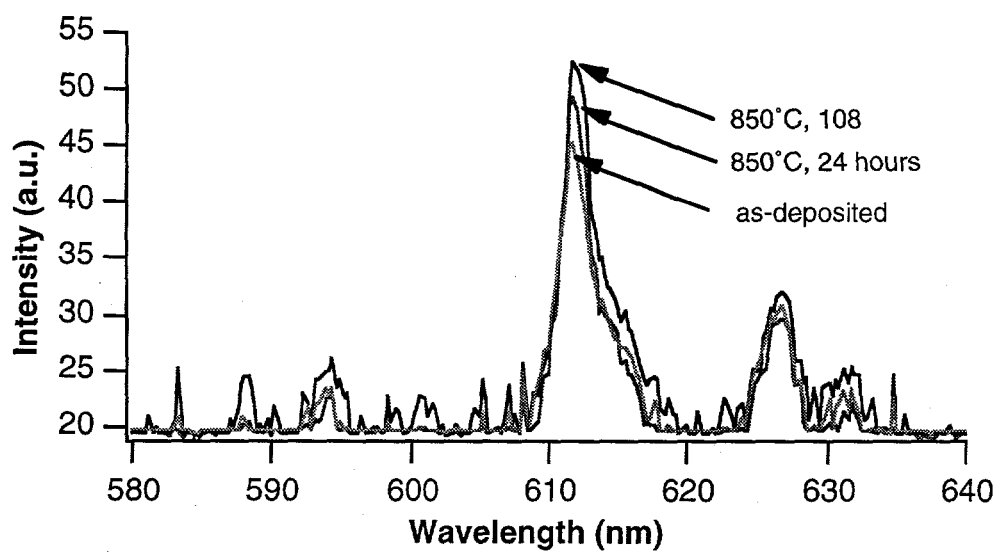
**Figure 10** SEM micrographs of the films deposited at 700°C for four hours, (a) 1000X, (b) 5000X and (c) 10,000X.



**Figure 11** Photoluminescent emission spectra of film deposited at 500 (six hours), 600 (four hours) and 700 °C (four hours).



**Figure 12** XRD spectra for the film grown at 600°C for eight hours and post-annealed at 850°C for 24 and 108 hours. The (400) and (420) reflections are shown.



**Figure 13** PL spectra of  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  films deposited for eight hours at 600°C and annealed at 850°C for 24 and 108 hours.