Cost-effective electrostatic-sprayed $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ phosphor coatings by using salted sol–gel derived solution

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Abstract. 3 Mol% of europium doped strontium aluminate ($\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$) coatings on silicon substrates were prepared by electrostatic spray deposition method using a salted sol–gel derived solution as a starting material. As-deposited films at 100°C for 5 h were heated at 1100°C for 2 h under a reducing ambient atmosphere of 95% N_2 + 5% H_2 . Nanocrystalline SrAl_2O_4 film was confirmed by surface morphological and crystallographic analyses. Monitored at 520 nm, the excitation spectrum showed a broad band from 300 ~ 500 nm and the emission intensity showed a maximum yellow peak intensity at 512 nm with a broad band from 460 ~ 610 nm.

Keywords. Strontium aluminate; electrostatic spray deposition; yellow peak.

1. Introduction

The Eu^{2+} -activated SrAl_2O_4 phase with tridymite-like structure was reported by many researchers to exhibit long, persistent and bright bluish-green phosphorescence and greater chemical stability than traditional sulphide-based ZnS:Cu , Co phosphors (Katsumata *et al* 1998; Choi *et al* 2006). SrAl_2O_4 has a stuffed tridymite-like structure (Escribano *et al* 2005) related to high- SiO_2 , built up layers of $[\text{SiO}_4]$ tetrahedra sharing corners that give rise to six-corner rings. In SrAl_2O_4 , Sr^{2+} ions are located in the cavities of the framework of $[\text{AlO}_4]^{5-}$ tetrahedra, occupying two different sites with low symmetry and coordinated by nine oxygen atoms.

The preparation of SrAl_2O_4 as single phase by solid-state reactions requires temperatures above 1900°C. It is, therefore, a technological issue to reduce the temperature of synthesis. In previous studies, Chergn and Chen (2001) proposed a sol–gel route for obtaining SrAl_2O_4 using alkyl borate as a source of flux as well as metal alkoxides precursor for the formation of SrAl_2O_4 at low processing temperature. Despite successes with the alkoxide route, the expense and moisture sensitivity of metal alkoxides limits its commercial applicability. Furthermore, chemical solution methods in preparing phosphorous coatings have rarely been

investigated and fabrication conditions have not been well established.

In order to prepare phosphorescent coatings, in this work, nanocrystalline $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ /silicon (Si) structures were synthesized by using a cost-effective electrostatic spraying deposition (ESD), and their properties of crystal structure and photoluminescence were examined.

2. Experimental

3 Mol% of europium-doped SrAl_2O_4 solutions were prepared by a further modification of already modified Pechini's method (Escribano *et al* 2005). The starting materials were aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), strontium acetate [$\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$], europium chloride ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), and ethanol as a solvent. The precursor was dissolved in ethanol for 24 h at 90°C. A small amount of acidic water (pH 1) was added in the Al and Sr solution to help dissolution and avoid precipitation of non-desired Al and Sr oxo-hydroxides. Finally, citric acid in molar ratio 1 ($\text{Sr} + \text{Al} + \text{Eu} : \text{citric acid} = 1 : 1$) was added at 90°C for 2 h.

The ESD has been commonly used to synthesize nano-sized particles and coatings of oxide materials. The working principles of the ESD have been described elsewhere (Hwang *et al* 2007). Briefly, in order to obtain a stable cone-jet mode of electrostatic atomization, high voltage (25 kV) was applied between the stainless needle tip and ground electrode by using d.c. power supply. The flow rate of the clear

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precursor solution was kept at 0.05 ml / 60 min by using a syringe pump and a substrate on ground electrode was heated at 100°C for 5 h. Coatings on Si(100) substrate were finally annealed at 1100°C for 2 h in N₂/H₂ atmosphere.

The thickness of the coatings, 1 ~ 1.2 μm, was measured using a step method (High-accuracy Digital Measuring Instrument, Litematic VL-50A, Mitutoyo Corp., Japan). Crystalline phase evolution was carried out with an X-ray diffractometer (XRD, D-Max-1200, Rigaku, Japan) with Bragg Brentano geometry using CuKα (λ = 1.54056 Å). The morphology and chemical composition of surface of the films was evaluated by field emission scanning electron microscope (FESEM, S-4700, Hitachi, Japan) and energy dispersive X-ray spectrometry (EDS). The excitation and emission spectra of the samples were recorded at room temperature using a fluorescent spectrophotometer (F4500, Hitachi, Japan) equipped with a Xenon lamp source. The decay curves were obtained at room temperature using a brightness meter (LS-100, Konica Minolta, Japan). Before decay curves measurement, the samples were exposed to standard 60 W Xenon lamps for 25 min. All measurements were carried out at room temperature.

3. Results and discussion

The surface microstructural morphology and chemical composition of the SrAl₂O₄:Eu²⁺ films prepared by ESD are shown in figures 1 (a) and (b), respectively. Generally, the particle size of SrAl₂O₄:Eu²⁺ powder prepared by the solid-state reaction is about several micrometers (Jia 2003), much larger than that of the chemical solution-derived powders. Figure 1(a) shows an evidence of coalesced nanoparticles. From the EDS result, strontium and aluminum ions as well as europium ion were detected on the surface of the film. Estimated value of the Sr/Al ratio for the coating was observed to be 1.92, which is slightly lower than the nominal value of 2.

Figure 2 shows XRD pattern of ESD derived SrAl₂O₄:Eu²⁺ films on Si substrate after annealing at 1100°C. It can be seen that the monoclinic SrAl₂O₄ phase (space group *P*₂₁) pattern is characterized by three peaks around 2θ = 28 ~ 29° (JCPDS No. 34-0379), and weak Sr₄Al₁₄O₂₅ (JCPDS No. 52-1876) as secondary phase. An estimation of the crystal size for the sample was performed using Scherrer's equation from the full width at half maximum (FWHM) of the most intense peak at 2θ = 28.44°. The calculated average size for the crystallite was about 60 nm. SrAl₂O₄ with a stuffed tridymite-like structure belongs to the monoclinic *P*₂₁ space group according to the literature (Clabau *et al* 2005). Sr²⁺ ions are located in the cavities of the framework of corner-sharing AlO₄⁵⁻ tetrahedra. Oxygen is shared with two aluminum ions so that each tetrahedron has one net negative charge. The charge balance is accomplished by the Sr²⁺ ions, which occupy interstitial sites within the tetrahedral framework. There are two kinds of low symmetric sites occupied by Sr²⁺. Because the sizes of Eu²⁺ (1.20 Å) and Sr²⁺ (1.21 Å) are very similar, readily substituted Eu²⁺ ion to the site of Sr²⁺ will not involve a significant distortion of the lattice parameter (Haranath *et al* 2003).

There are two phases in SrAl₂O₄, a high-temperature hexagonal phase (space group *P*₆₃22) and a low-temperature monoclinic phase. The transition temperature occurs at 650°C (Avdeev *et al* 2007). Since only the monoclinic form shows luminescent properties when doped with rare earth ions, the characterization of the polymorph content in a sample is of great importance. However, according to JCPDS files 34-0379 for the monoclinic and 32-1336 for the hexagonal polymorph, the (102) hexagonal reflection overlaps the monoclinic (220) peak, while the monoclinic (−211) is not superposed to any hexagonal reflection (Escribano *et al* 2005). Henderson and Taylor (1982) proposed to use the parameter in order to quantify the proportion of monoclinic and hexagonal phases.

$$R = -211_{\text{mon}} / (220_{\text{mon}} + 102_{\text{hex}}).$$

Figure 1. (a) FE-SEM image and (b) EDS graph for SrAl₂O₄:Eu²⁺ films annealed at 1100°C.

Figure 2. XRD pattern of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ films annealed at 1100°C .

Figure 3. Excitation (a) and emission (b) spectra for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ films annealed at 1100°C .

In this equation, -211_{mon} and 220_{mon} stand for the intensities of the monoclinic polymorphs and 102_{hex} is the intensity of the highest peak of the hexagonal polymorph. R aims to establish the ratio between monoclinic and hexagonal polymorphs. If only the monoclinic polymorph is present, the R value should be ~ 1.09 , while $R < 1.09$ would indicate an increase in the hexagonal phase content. Estimated R value was 1.123, relatively higher than the nominal value for the monoclinic polymorph of 1.09. We assumed that the (102) and (110) hexagonal reflections probably overlapped the monoclinic (220) and (002) peaks, respectively.

Figure 3(a) shows the excitation spectrum of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ films annealed at 1100°C monitored from 300 nm to 500 nm. A broad band with a maximum at around 360 nm was observed. This broad band corresponded to Eu^{2+} electron transition lying in the bandgap region of the host matrix. It is well known that the emission spectra of

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ have a broad band characteristic due to $4f-5d$ transitions of Eu^{2+} ion, and the emission peak is at about 520 nm resulting in a green light (Katsumata *et al* 1998; Escribano *et al* 2005; Choi *et al* 2006).

In general, it can be said that there are two basic factors that influence the emission radiation of a phosphor. The first one is the strength of the crystal field at the sites of the luminescent ions, and the second is the degree of covalence of these ions with the surrounding oxygen ions. The role of the crystal field is to split the $5d$ level into sublevels; the luminescence always takes place from the lowest sublevel (Haranath *et al* 2003).

Figure 3(b) depicts the emission spectrum of the prepared films monitored for 360 nm excitation. A broad emission peak was observed at around 512 nm, revealing the characteristic emission of Eu^{2+} activators ($4f^65d^1 \rightarrow 4f^7$). Additional weak emission peak due to Eu^{3+} transitions was observed at around 625 nm. Compared with the phosphors obtained from conventional solid-state reaction (Jia 2003), the emission maximum band of the film shifts from 520 to 512 nm. The slight blue shifts in the emission band may be attributed to the changes of the crystal field around Eu^{2+} arising from the nano-sized particles. Since the excited $4f^65d^1$ configuration of Eu^{2+} ion is highly sensitive to the lattice environment and $5d$ electron can be strongly coupled with the lattice, the mixed states of $4f$ and $5d$ will be split by the crystal field, which may lead to the shift of the emission peak toward shorter wavelength. Zhang *et al* (2009) reported that the particles with nanometer size make the surface energy to increase, which causes change of the crystal field around the local environment of Eu^{2+} . These reasons may lead to the blue-shift in its emission peak.

The afterglow characteristics were measured for the nanocrystalline $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ coating and the commercially available $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, Dy^{3+} powder (G-300, LumiNova)

Figure 4. Afterglow decay curves of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ films and commercial $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ powder as a reference.

as a reference (figure 4). The phosphorescence intensities at 520 nm were plotted as a function of lasting time. It can be seen from the curves that the sample showed a rapid decay and then long lasting phosphorescence afterward. The phosphorescence intensity for the nanocrystalline $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ coating can be detected to 23 mcd/m² at 60 min. Both the initial intensity after excitation and the afterglow intensity of the commercial powder were higher than nanocrystalline $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ coating. The difference is simply attributed to the Dy^{3+} ions distribution in the commercial powder. The Dy^{3+} incorporation creates deep traps in the form of hole trapping levels near the valence band. Therefore, when the excitation source is switched off, the relaxation of these secondary ions from deep traps is very slow; this leads to the long persistence of phosphor. In our case, both the concentration of the trap and the coexistence of Eu^{3+} ions in the coating are quite different from commercial powder. The doping

of the second rare-earth ions and the perfect reduction are still being studied in-depth.

4. Conclusions

In summary, nanocrystalline $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ coatings annealed at 1100°C were prepared by ESD method in this experiment. This synthesis temperature and the crystal size, 60 nm, of the coatings were much lower and smaller than those obtained in the conventional solid-state method. The diffraction patterns were dominantly due to monoclinic SrAl_2O_4 phase and other crystal phases such as hexagonal polymorphs and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ could be detected. The slight shift of main peak of emission at 512 nm toward shorter wavelengths for the coatings occurred due to the decrease in particle size.

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