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Ceramics International 30 (2004) 2029–2031

CERAMICS INTERNATIONAL

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Luminescence characteristics of $SrTiO_3$:Pr,Ga phosphor synthesized by sol–gel process

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Received 1 December 2003; accepted 23 December 2003

Available online 26 June 2004

Abstract

The thin film phosphors of $SrTiO_3$:(0.004 mol Pr, 0.02 mol Ga) have been prepared by chemical solution deposition (CSD) method on the SiO_2/Si, alumina, and quartz substrates. The phase formation and photoluminescence (PL) property of thin films with crystallization temperature have been characterized by FE-SEM, XRD, and spectrophotometer. The $SrTiO_3$ (ST) phase was formed from 600 °C regardless of the type of substrate. The emission peak (611 nm) and excitation peak (370 nm) from the thin films were similar to those of the powder sample prepared by solid-state reaction. The SiO_2/Si substrate produced the strongest emission and excitation spectra.

Keywords: A. Sol–gel processes; C. Optical properties; D. Perovskites; E. Lamp envelopes

1. Introduction

Luminescent thin films have been drawn interest due to their potential applications in flat panel displays and LED phosphors [1–3]. The oxide perovskite $SrTiO_3$ (ST) is expected to be chemically stable and a good candidate for optical host materials. Several studies already have been reported on the luminescence of Pr^{3+} doped $SrTiO_3$ powder samples. The addition of Al^{3+} or Ga^{3+} into $SrTiO_3$:Pr^{3+} have been reported to greatly enhance the emission intensity. The Pr^{3+} luminescence center can be excited by electron and ultraviolet (UV) ray to produce either green or red emission ($^3P_0 \rightarrow {}^3H_4$ or $^1D_2 \rightarrow {}^3H_4$) depending on the host materials [3–7,9]. Sol–gel process has been applied for thin film phosphors in $BaTiO_3$:Eu^{2+} [5], Zn_2SiO_4:Re^{3+} [1], and $Eu_xY_{2-x}SiO_5$ [8]. In this study the $SrTiO_3$ thin films co-doped by Pr (0.004 mol) and Ga (0.02 mol) have been prepared by chemical solution deposition (CSD) method and the photoluminescence (PL) characteristics have been analyzed.

2. Experimental

The precursor solution has been prepared by DNF solution Co. as followings. High purity praseodymium(III) acetate hydrate [$(CH_3CO_2)_3Pr{\cdot}xH_2O$, 99.9%], gallium(III) acetylacetonate ([$CH_3COCH{=}C(O–)CH_3]_3Ga$, 99.99%) and strontium(II) acetate [$(CH_3CO_2)_2Sr$, 99.995%] were used as the source of Pr, Ga, and Sr. Acetic acid was added to the mixture of the above three solutions. The titanium source was added as the last step using the titanium(IV) bis(ammonium lactato) dihydroxide (50 wt.% solution in water and $[CH_3C(O–)CO_2NH_4]_2Ti(OH)_2$).

The precursor solution was spin-coated on the substrate at a speed of 5000 rpm. Three different types of substrates, i.e., alumina, quartz, and SiO_2/Si, have been used in this study since the photoluminescence of thin films have been reported as substantially dependent on the surface morphology and crystallinity. The spin-coated liquid film was dried at 200 °C on a hot plate. To increase the thin film thickness the above processes were repeated by 10-times. The coated thin films were crystallized in the temperature range of 500–1000 °C for 30 min in air.

Surface morphology and phase formations have been characterized by FE-SEM (Hitachi 4300) and high resolution XRD (Phillips HR-XRD). The excitation and

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0272-8842/$30.00
doi:10.1016/j.ceramint.2003.12.200

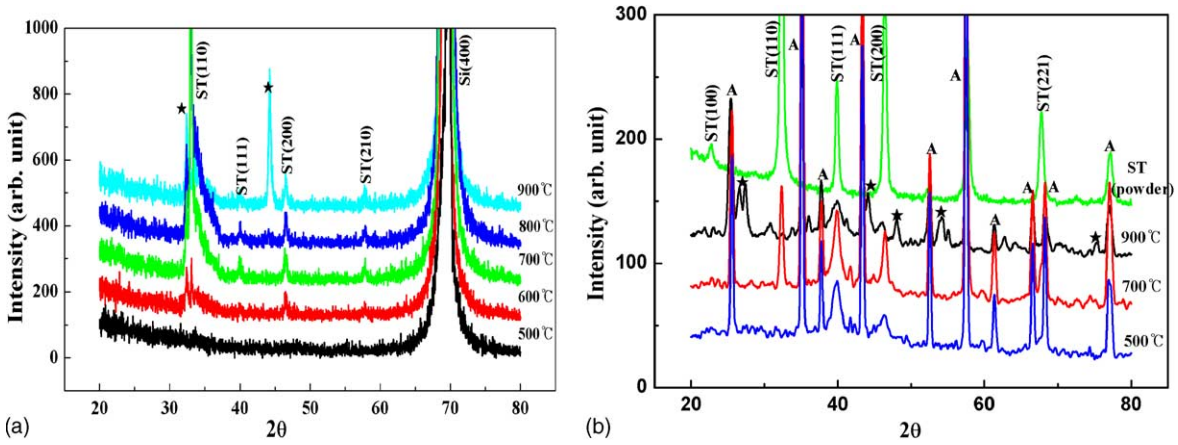

Fig. 1. XRD patterns of thin films deposited on: (a) SiO_2/Si substrate and (b) alumina substrate with crystallization temperature.

emission spectra were recorded using PL spectrophotometer (Aminco-Bowman Co.).

3. Results and discussion

The XRD patterns of the thin films deposited on the SiO_2/Si and alumina substrates after crystallization are shown in Fig. 1(a, b). The $SrTiO_3$ phase begins to form from 600 °C on the SiO_2/Si substrate while from 500 °C on the alumina substrate. The peak intensity of ST phase increases with temperature. At 900 °C the thin film reacts with the substrates and forms an unknown impurity phase (marked by ★). Fig. 2 shows the FE-SEM images of the thin films on the SiO_2/Si substrate (a, b) and quartz substrate (c, d) crystallized at 700 °C. The sintered surfaces are shown in the (a) and (b). The fractured cross-sections are shown in the (b) and (d).

The effect of crystallization temperature on the PL of the thin films on the SiO_2/Si substrate is shown in Fig. 3. The emission peak from the Pr^{3+} does not change with the extrinsic condition such as crystallization temperature. The emission intensity of $^1D_2 \rightarrow {}^3H_4$ (611 nm) shows a max. value at 600 °C then decreases with increasing temperature. This emission peak disappears at 1000 °C, which is ascribed to the formation of the impurity phase and the decrease of the ST phase as shown in Fig. 1.

The excitation spectra of ST thin films on the SiO_2/Si also show a max. intensity at 600 °C then decrease with temperature. The excitation spectra for thin film on the SiO_2/Si locate at 370 nm. These emission and excitation peak positions are similar to those of the $SrTiO_3$:Pr,Ga prepared by solid-state reaction method (Ex.: 355 nm, Em.: 615 nm) [4]. Effect of the substrate type on the intensity of PL spectra is represented in Fig. 4. The thin films were crystallized at 800 °C in air. The SiO_2/Si substrate showed the strongest

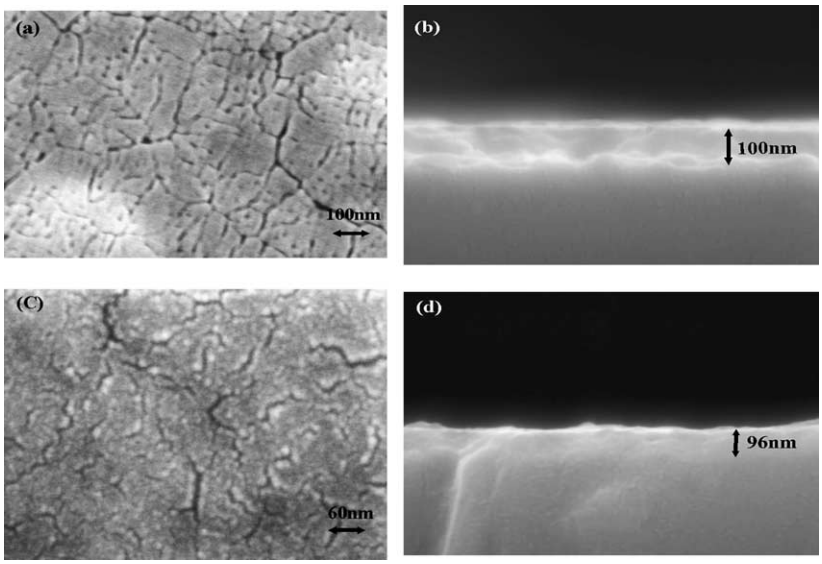

Fig. 2. SEM images of thin films on SiO_2/Si (a, b) and quartz (c, d) substrates crystallized at 700 °C (sintered surfaces (a, c) and fractured cross-sections (b, d)).

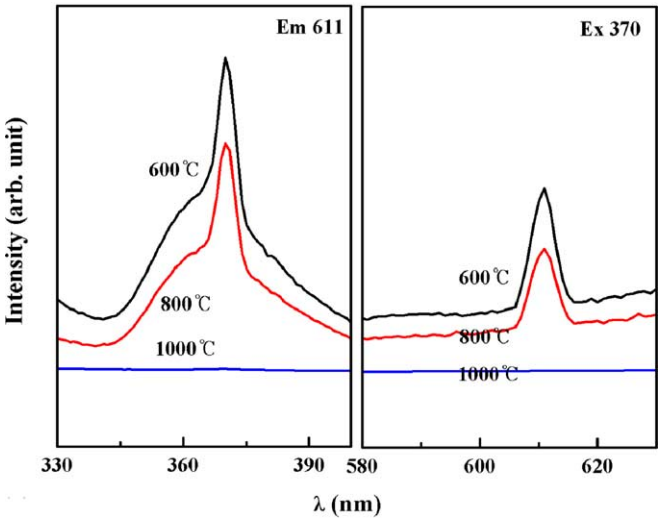

Fig. 3. Effect of crystallization temperature on PL of thin films on SiO_2/Si substrate.

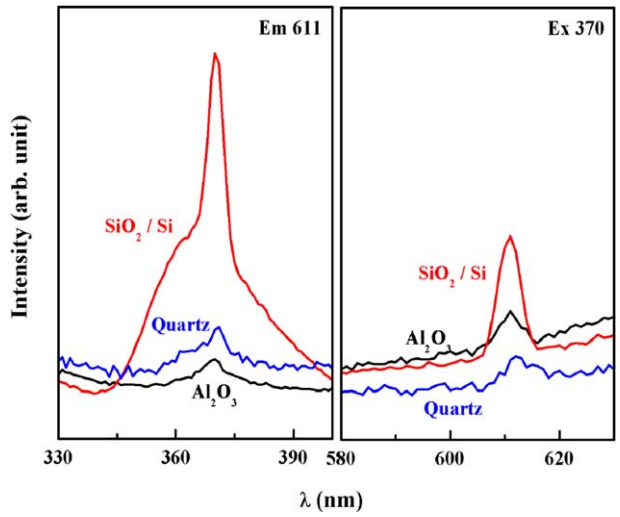

Fig. 4. Effect of substrate on PL intensity of thin films crystallized at 800 °C in air.

emission and excitation spectra while the quartz substrate led to the lowest spectra intensity.

The thin film thickness, surface morphology, and ST phase formation of the thin films on the different type of substrates are similar as shown in Figs. 1 and 2. Nevertheless the PL intensity has been greatly enhanced in the thin films on the SiO_2/Si substrate. The mechanism for the enhancement of PL intensity from the SiO_2/Si substrate needs to be studied further.

4. Conclusion

The thin film phosphor of $SrTiO_3$:(Pr,Ga) have prepared by CSD method and PL property have been analyzed. The ST phase was formed at 600 °C regardless of the type of substrate. The thickness of thin films was in the range of 95–110 nm. The emission (611 nm) and excitation (370 nm) peaks from the thin films showed similar values to those of the powder sample prepared by solid-state reaction. The SiO_2/Si substrate produced the strongest emission and excitation spectra while the quartz substrate led to the lowest spectral intensity. The PL characteristics were deteriorated as the crystallization temperatures increases to above 800 °C. The mechanism for the superior PL characteristics from the SiO_2/Si substrate needs to be studied further.

Acknowledgements

This work was supported by the grant from Hoseo SERC (Regional Research Center supported by KOSEF).

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