

以溶膠-凝膠法製備 $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ 薄膜與特性之研究 Preparation and Characterization of $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ Films by Sol-Gel Deposition

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摘要

本研究使用溶膠-凝膠法來製備 $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS)薄膜，並使用X光繞射、掃描式電子顯微鏡、X光光電子光譜與光致發光光譜儀來檢測薄膜特性。經旋鍍後的非晶質薄膜可以使用 1200°C 退火而結晶並具有LGS(110)優選取向。在光致發光光譜儀中，使用381nm為激發光源可使LGS薄膜發出429nm波長的光。此發光來源推測為 Ga^{3+} 離子佔據晶格的八面體位置所導致，且此發光現象會隨著退火時間的增加而有降低的趨勢。在本文中，將近一步討論LGS薄膜的發光機制與結晶結構關係。

關鍵詞： $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ，薄膜，結晶化，溶膠凝膠旋鍍法，光致發光

Abstract

A simple sol-gel deposition was employed to prepare $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS) films which were characterized by X-ray diffraction, scanning electron microscopy images, X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) measurements. The as-deposited LGS films were amorphous and induced to crystallize with (110) preferred orientation by annealing at 1200°C . A blue emission peak of the films by PL measurement was found at 429 nm when excited at 381nm. The blue PL emission of the films was suggested originated from the Ga^{3+} at the octahedral sites. The luminescent intensity of LGS films would be decreased when the annealing times increased. The relationship between the mechanism of luminescence and the crystalline structure of the LGS films are discussed.

Keywords: $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, thin films, crystallization, sol-gels spin coating, photoluminescence

I. INTRODUCTION

For the new coming wide-band code division multiple access (W-CDMA) system, the necessity desires a new piezoelectric material which has the acoustic properties between quartz and lithium niobate (LiNbO_3). $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS) that is one of the new piezoelectric materials grown in Russia from 1980s has larger electro-mechanical coupling factor (three times as large as quartz) and a zero temperature coefficient for resonant frequency [1-6]. Besides, LGS has no phase transition up to its melting point (1470°C). Because above excellent properties, LGS shall be a proper material for intermediate frequency surface acoustic wave (IF-SAW) filter fabricating in the

new generation communication system.

To date, most of papers have mainly discussed growth processes and piezoelectric properties of LGS bulks by Czochralski technique. It has been reported that high quality LGS-type crystals and films were prepared using liquid phase epitaxy (LPE) method [7-11]. The sol-gel process is an attractive method because of its precise composition control, low processing temperature, and ease of scaling-up for large-size substrates using spin coating and dip coating. In this paper, we report the successful preparation of preferred orientation LGS (110) films on SiO_2/Si , using the sol-gel method and post-annealing. And, it was found that these films showed photoluminescence characteristics from the experiment.

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II. EXPERIMENTAL PROCEDURE

The precursor solutions were prepared by dissolving Lanthanum chloride (LaCl_3), Gallium chloride (GaCl_3) and Tetraethoxysilane (TEOS) with molar ratio 3:5:1 in pure ethyl alcohol. The molar concentration of the formula species in solution is 0.6M. The solution was constantly stirred for over 72 hours to make it more homogeneous. A p-type Si (111) wafer with about 200nm thickness of silicon-oxide layer was used as the substrate. Thin films were obtained by spin-coating the precursor solution on the SiO_2/Si (111) substrate with two steps spinning as 1000 rpm for 7s and 3000 rpm 120s. The films were then heated at 300°C for 10 min to remove the organics. The coating/heating operations were repeated four times to obtain the desired thickness of the films. Finally, these films were annealed in air at 1200°C for different annealing time with a heating rate of 10°C /min and then cooled to room temperature.

Phase characterization of the film were examined by 1° grazing angle scan mode using XRD (MAC Science, M21X) $\text{CuK}\alpha$ radiation with 40kV and 200mA. The microstructure and chemical compositions of the films were analyzed using SEM/EDX (JOEL5600). The photoluminescence (PL) properties of the samples were conducted at room temperature on a Perkin-Elmer luminescence spectrometer (model LS 50B). X-ray photoelectron spectroscopy (XPS) was recorded by a VG Scientific ESCALAB 250 spectrometer with Al and Mg X-ray sources in the energy range from 1400 to 0 eV. The $\text{La}3d$, $\text{Ga}3d$, $\text{Si}2p$ and $\text{O}1s$ were measured and energy calibration was made versus the $\text{C}1s$ peak at 285 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows the typical SEM photograph of the fractured cross-section of the LGS films annealed at 1200°C for 5h. The thickness of LGS films was about 1.1 μm . From the photograph, the LGS films showed very uniform and no layers separation was observed for multi-coating.

Figure 2 shows the XRD patterns of the LGS films annealed at 1200°C with different time. The as-deposited LGS film was amorphous and the LGS film after 300°C was still amorphous as seen in Figure 2(a). The films show the LGS crystalline phases when the films were annealed at 1200°C for 3h as in Figure 2(b). The diffraction peak was identified as langasite (110) reflection indexed by ICDD card 41-155. Only the (110) reflection peak observed from the XRD patterns indicated that the LGS films with preferred orientation were obtained. When the annealing times increased from 3h to 10h, the (110) reflection peak still presented the preferred orientation and its FWHM decreased. It was reported that the formation of LGS crystals could only take place at near the melting temperature (~1470 °C) due to the complex chemical composition of LGS crystal and the incongruent in melt

[5]. The problem with the complex chemical composition can be overcome by the sol-gel process. This was evidence by the single phase (langasite) forming without second phase through crystallization.

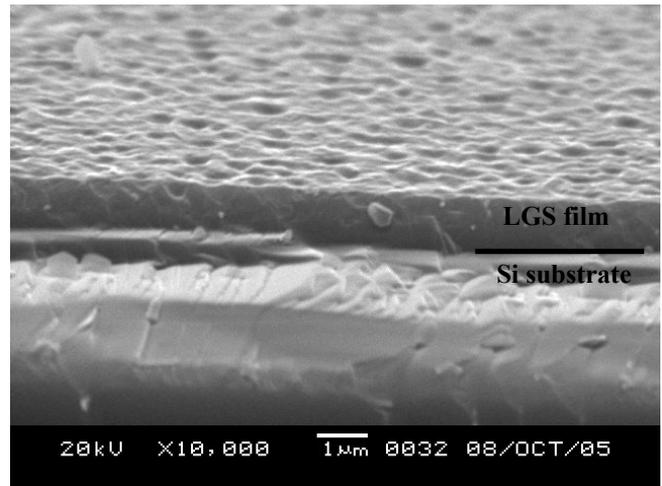


Fig. 1 Cross-section for films pre-heated at 300°C/10min and annealed at 1200°C/5hrs. The thickness of films is about 1.1 μm .

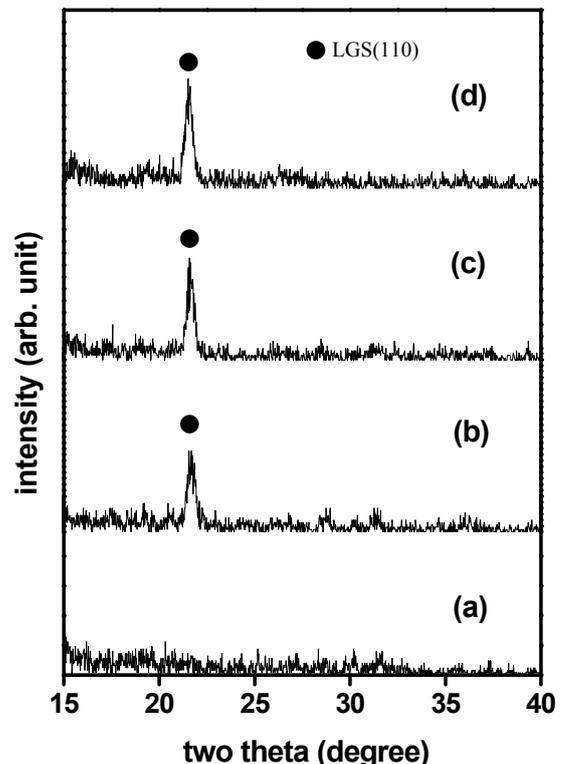


Fig. 2 XRD patterns of LGS films annealed at (a) 300°C /10min and 1200°C with different time (b) 3hrs, (c) 5hrs and (d) 10hrs.

Figure 3 shows the room temperature photoluminescence (PL) spectra of the LGS films annealed at 1200°C in wavelength range of 300-500nm. The emission peak of the films was found to be 429 nm under the excited light of $\lambda_{ex}=300\text{nm}$ as in Figure 3(a). The most strong absorption light was found to be $\lambda_{ex}=381\text{nm}$ for the emission light of 429 nm as in Figure 3(b). Therefore, the emission light at 429 nm has the strongest intensity when the excited light was set to be at 381nm as in Figure 3(c). Figure 4 shows the PL of the films versus the annealing time. It was found that a blue emission peak at 429 nm was observed at all spectra and the intensity of the emission light decreased as the annealing time increased. In the literatures, ZnGa_2O_4 , a well-known blue emission phosphor, has the absorption band peaking at 260 nm and the fluorescence at 432 nm that is possibly due to the octahedral Ga-O groups in the spinel structure [12-15]. Even though Ga^{3+} ions are distributed randomly in both tetrahedral and octahedral sites in spinel solid solution by other ions doping, the ZnGa_2O_4 is still fluorescent near 432 nm [12]. However, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS) that has a langasite-type crystal structure with space group P321 is different to ZnGa_2O_4 spinel [6]. The structural formula of LGS is $\text{A}_3\text{BC}_2\text{D}_4\text{O}_{14}$. A and B represent a dodecahedral site coordinated by 8 oxygen atoms and octahedral site coordinated by 6 oxygen atoms, respectively. Both C and D represent tetrahedral sites coordinated by 4 oxygen atoms, whereby the size of the D site

is slightly smaller than that of the C site. In LGS, La^{3+} occupies A site, Ga^{3+} locates B, C and half of D sites and Si^{4+} the unfilled D sites. Therefore, the LGS broad emission at 429 nm can be ascribed to the self-activated centers origination from the octahedral Ga-O group in the langasite-type crystals and is similar to that of ZnGa_2O_4 crystal. The difference in absorption band between 381 nm of LGS and 260 nm of ZnGa_2O_4 was speculated that Ga-O bondings in octahedral sites were distorted by LGS complex crystal structure.

X-ray photoelectron spectroscopy spectra of $\text{Ga}^{3+}3d$ and $\text{O}^{2-}1s$ in the annealed LGS films at 1200°C with different annealing times are depicted in Figure 5 and Figure 6, respectively. The binding energy of $\text{Ga}^{3+}3d$ did not change apparently, however, the binding energy of $\text{O}^{2-}1s$ varied as the annealing time increased. The binding energy of $\text{O}^{2-}1s$ increased from 532.8 to 533.2 eV as the annealing time increasing from 3h to 10h. Comparing the XPS results with the PL results, it was found that the films with lower binding energy of $\text{O}^{2-}1s$ would have high intensity of emission. The increase in the binding energy of $\text{O}^{2-}1s$ was suggested due to increasing the concentration of oxygen vacancies as reported [15]. Some authors implied that the phosphor had stronger emission intensity with higher concentration oxygen vacancies [12,15]. Therefore, we can speculate that the increasing annealing times would conduce the oxygen vacancies decreased according to the XPS spectra. The higher intensity of the PL emission of the films can be related to the higher concentration of oxygen vacancies during annealing with shorter times.

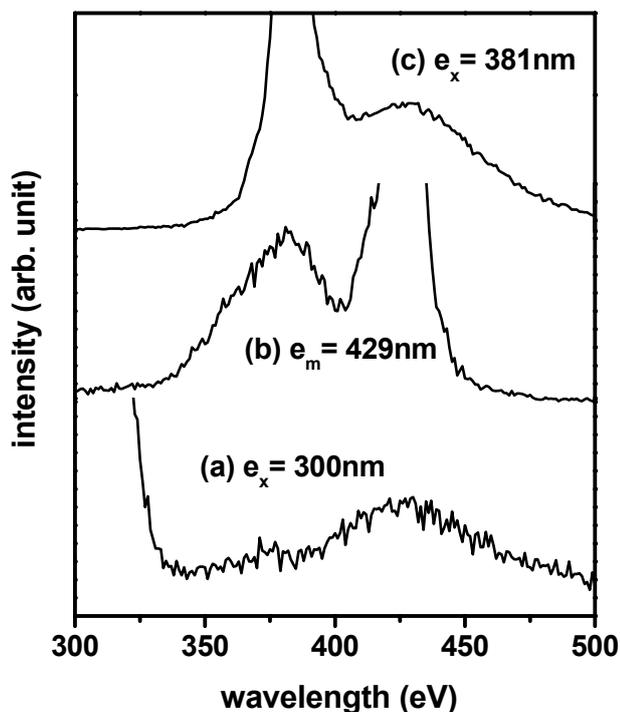


Fig. 3 The photoluminescence characteristics of the LGS films annealed at 1200°C. (a) emission spectrum under $\lambda_{ex}=300\text{nm}$. (b) the absorption spectra by setting $\lambda_{em}=429\text{nm}$. (c) emission spectrum under $\lambda_{ex}=381\text{nm}$.

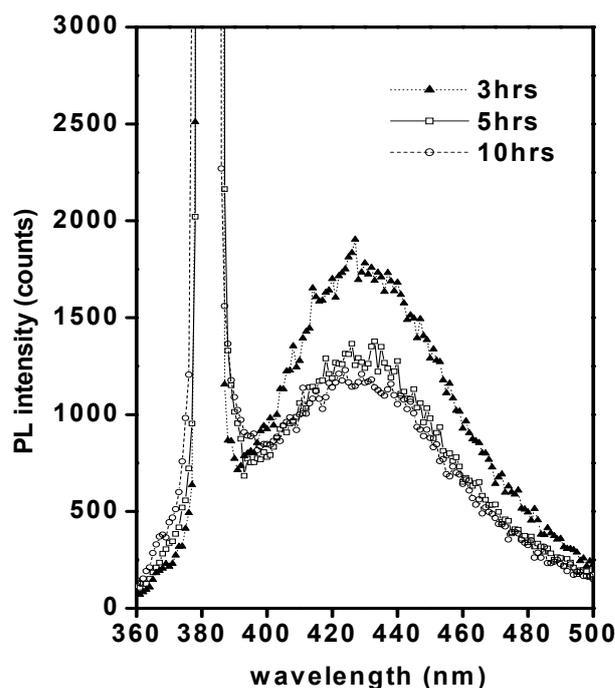


Fig. 4 The PL emission of the films under $\lambda_{ex}=381\text{nm}$ versus the annealing temperature. (a) 3hrs, (b) 5hrs, (c) 10hrs at 1200°C

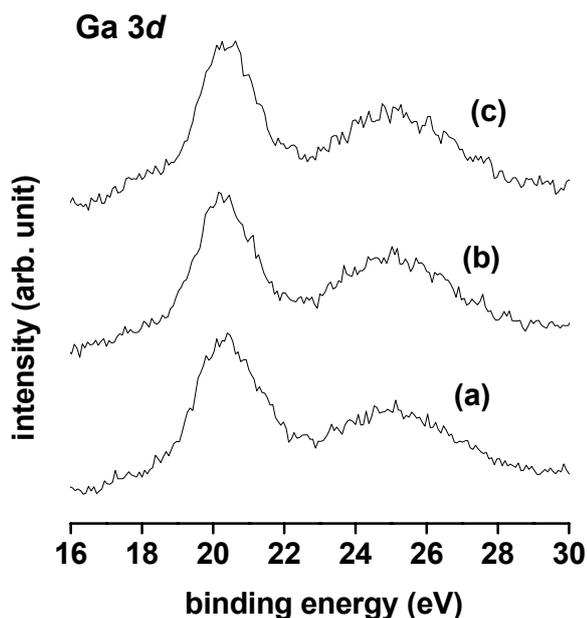


Fig. 5 X-ray photoelectron spectroscopy spectra of Ga^{3+} 3d of LGS films annealed at 1200°C for (a) 3hrs, (b) 5hrs and (c) 10hrs.

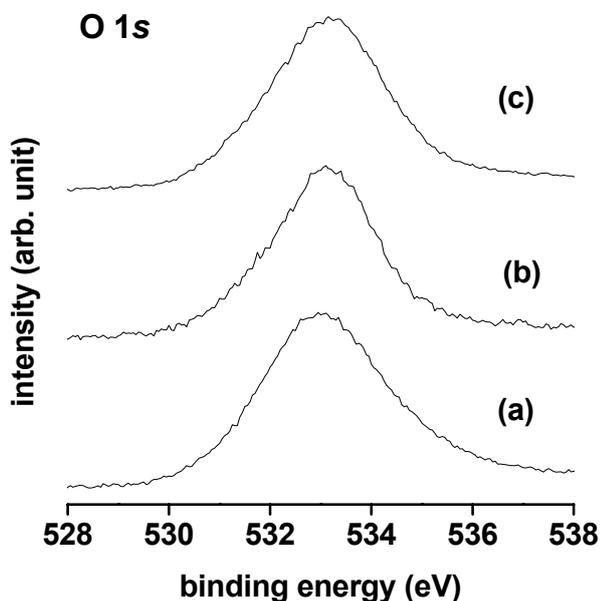


Fig. 6 X-ray photoelectron spectroscopy spectra of O^{2-} 1s of LGS films annealed at 1200°C for (a) 3hrs, (b) 5hrs and (c) 10hrs.

IV. CONCLUSION

$\text{La}_3\text{Ga}_5\text{SiO}_{14}$ (LGS) films were prepared by the sol-gel spin coating with the stoichiometric metal chloride. This is the first time to obtain photoluminescence spectra in the LGS films. The PL emission spectra of the LGS films show a blue emission at $\lambda_{\text{em}}=429\text{nm}$ under $\lambda_{\text{ex}}=381\text{nm}$. The PL intensity decreased should be related to the concentration of oxygen vacancies decrease as the annealing time increased at 1200°C .

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