Effects of oxygen pressure on La$_3$Ga$_5$SiO$_{14}$ thin films grown by pulsed laser deposition

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Received 9 December 2009; revised 15 March 2010

Abstract: La$_3$Ga$_5$SiO$_{14}$ thin films were grown on Si (100) substrates by pulsed laser deposition at several oxygen pressures (5, 10, and 20 Pa). The effects of oxygen pressure on the structural and morphological characteristics of the films were investigated using X-ray diffraction, atomic force microscopy, and scanning electron microscopy. X-ray diffraction results showed the intensity of lines from crystallites oriented along the (300) and (220) planes increased as the oxygen pressure was increased to 20 Pa. The deposited films exhibited smooth surface as observed by atomic force microscopy and scanning electron microscopy. Photoluminescence measurements with 260 nm excitation showed that the films had emission in the ultraviolet and blue regions, and the luminescence intensity of the films increased with increasing oxygen pressure. We propose that these emissions originated from self-activated luminescence centers in the tetrahedral and octahedral Ga–O groups.

Keywords: thin films; pulsed laser deposition; crystal structure; surfaces; rare earths

Crystalline langasite (La$_3$Ga$_5$SiO$_{14}$, LGS) has been extensively studied as a promising nonferroelectric piezoelectric material, although Kaminsky first reported it as a laser crystal in 1983[1]. LGS belongs to the trigonal system, and has the Ca$_3$Ga$_2$Ge$_4$O$_{14}$ structure. Its piezoelectric properties are intermediate between those of quartz and LiNbO$_3$[2,3]. Compared with quartz, LGS has a higher electromechanical coupling coefficient and better frequency stability[4] for both bulk (BAW) and surface acoustic wave (SAW) applications. Moreover, LGS has no phase transition in the range from room temperature up to its melting point (1470 °C)[3], which allows its application not only at low but also at high temperatures.

Until now, LGS materials are mainly grown as single crystals using the Czochralski or vertical Bridgman method[4,5]. With the rapid development of modern communications techniques, electronic devices are required to have smaller size and operate at higher frequencies that demand a piezoelectric material in the form of a thin film. Previous research has reported on the production of LGS thin films by liquid phase epitaxy (LPE), the sol-gel process, and radio frequency (RF) sputtering[6–9]. However, there are few reports on the growth of LGS thin films by pulsed laser deposition (PLD). Compared with the above mentioned methods, PLD is a versatile technique that can be used to grow complex multicomponent oxide thin films with oriented or epitaxial structure[10,11]. In this paper, we reported the growth of LGS thin films on Si substrates by PLD. Effects of oxygen pressure on the structural, morphological, and luminescence properties of the deposited films were studied.

1 Experimental

1.1 Preparation of LGS thin films

LGS thin films were deposited on Si (100) substrate by pulsed laser deposition (Lambda Physik COMPEX 201 series) with the excitation by a KrF excimer laser (248 nm, 20 ns, 20 Hz). The energy density at the target was maintained at ~4 J/cm$^2$. The target used was a 50 mm×3 mm single crystal LGS disk grown by our group[12], and rotated at 35 r/min during the deposition process to avoid surface pitting. Before deposition, the silicon substrate was cleaned in an ultrasonic bath for 10 min in acetone, ethanol, and deionized water in sequence. The distance between the target and substrate was 4.5 cm. The chamber was evacuated to a base pressure of 5×10$^{-3}$ Pa prior to deposition, and then oxygen (99.99% purity) was introduced at several pressures (5, 10 and 20 Pa) with a mass flow meter while the vacuum pump was working. The substrate temperature was 400 °C and the deposition time was 30 min for all LGS films. After deposition, the substrate was cooled down to room temperature at oxygen atmosphere.

1.2 Characterization of LGS thin films

The thickness of the deposited films was measured by a...
Tencor Alpha-step surface profiler (Kosaka ET-350). The structural properties were analyzed by an X-ray diffractometer (Rigaku D/Max-2000pc) using Cu Ka radiation ($\lambda=0.154$ nm). The surface morphology of the deposited films was observed by an atomic force microscope (AFM, Veeco D3100) in contact mode, and by a scanning electron microscope (SEM, Hitachi S-4800). The stoichiometry data were obtained by an energy dispersive spectrometer (EDS, Horiba EMAX Energy, EX-350). The photoluminescence (PL) properties were recorded on a fluorescence spectrophotometer (Edinburgh FLS920). All measurements were performed at room temperature.

2 Results and discussion

2.1 XRD analysis

Fig. 1 shows the XRD patterns of LGS thin films deposited at 400 °C with different oxygen pressures ranging from 5 to 20 Pa. Except for the Si (200) diffraction peak, the single-phase films exhibit only two peaks located at $2\theta=38.2^\circ$ and $44.4^\circ$, indexed as the (300) and (220) diffraction peaks of the LGS phase, respectively. The intensity of the two diffraction peaks increases at higher oxygen pressure, indicating that high pressure is beneficial to larger grains and better crystallinity. In addition, a diffuse background peak ranging from 25° to 35° appears only for the film grown at 5 Pa, which indicates that a certain amount of amorphous structure is present. This non-crystallinity is present because the deposited materials did not have sufficient time for the deposited atoms to rearrange themselves into a preferred orientation before being covered by a new layer, as indicated by higher deposition rates at lower pressure (Table 1). In contrast to the diffraction peak intensity ratio of 121/49 $\pm 2.5$ between the (300) and (220) peaks indicated by the standard PDF card, the measured ratio is close to unity for the LGS thin film deposited at 20 Pa. This comparison indicates that LGS film growth favors the (220) orientation. Compared to the LPE and RF methods,[6–9] PLD shows an advantage of a lower crystallization temperature. Nevertheless, it should be noted that the diffraction intensity of the films is weak, even though a high-power XRD apparatus was used. This result is an indication that growing high quality crystalline LGS films is not a simple task with PLD.

2.2 AFM and SEM analysis

To improve the piezoelectric performance of the film and the quality of the electrodes deposited on the film, the surface of such a film should be very smooth. The AFM images of the LGS films grown at different oxygen pressures are shown in Fig. 2(a–c). All the films present a smooth surface. The measured root mean square roughness ($R_{\text{rms}}$) of the films grown at 5, 10, and 20 Pa is about 0.30, 0.43 and 0.74 nm, respectively. The grain size of the deposited films becomes larger with increasing oxygen pressure, consistent with the XRD results (Fig. 1). We also observed the surface and cross-section morphology of the LGS film prepared at 20 Pa with SEM (Fig. 2(d)). The SEM image shows that the deposited film has a uniformly smooth surface. Dense structure without layer separation is observed in the cross-section image.

2.3 Chemical composition analysis by EDS

Additionally, the chemical composition of the LGS film grown at 400 °C and 20 Pa was analyzed by EDS, shown in Table 2. Considering that the detection depth of EDS is about 1 μm, the Si component of substrate is counted too, so the Si content is not listed. All the three calculated atomic ratio of La to Ga are close to 3:5, so it is assumed that the composition of deposited films is consistent with the target La$_3$Ga$_5$SiO$_{14}$.

2.4 PL spectra analysis

The room temperature PL spectra of LGS thin films deposited at different oxygen pressures are presented in Fig. 3. The PL spectra of all the deposited films show a broad emission band from 300 to 500 nm, with two split peaks for the thin film grown at 20 Pa. Moreover, the PL intensity of the LGS films increases at higher oxygen pressures that can be attributed to improved crystallinity.

As reported in Ref. [9], the PL emission of LGS films is

Table 1 Thickness and the deposition rate of the LGS thin films deposited at different oxygen pressures

<table>
<thead>
<tr>
<th>Oxygen pressure/Pa</th>
<th>Thickness/μm</th>
<th>Deposition rate/(nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>510</td>
<td>17.0</td>
</tr>
<tr>
<td>10</td>
<td>371</td>
<td>12.4</td>
</tr>
<tr>
<td>20</td>
<td>340</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Table 2 Calculated atomic ratios of La and Ga element in LGS film (The ‘NO.’ represents the different measured areas of the film, which was selected by random)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ga content/at.%</th>
<th>La content/at.%</th>
<th>atomic ratio of La to Ga</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.44</td>
<td>8.40</td>
<td>3:0:5.1</td>
</tr>
<tr>
<td>2</td>
<td>14.78</td>
<td>8.49</td>
<td>3:0:5.2</td>
</tr>
<tr>
<td>3</td>
<td>15.04</td>
<td>8.92</td>
<td>3:0:5.0</td>
</tr>
</tbody>
</table>
very similar to that of \( \text{ZnGa}_2\text{O}_4 \) with the blue emission around 432 nm and UV emission around 360 nm. The former is related to \( \text{Ga}^{3+} \) ions located at the octahedrally coordinated sites\(^{13,14}\). For the UV emission, Jeong et al. speculated that the origin is self-activated optical centers related to tetrahedral \( \text{Ga–O} \) groups\(^{15}\), while Kim et al. suggest that it originates from the \( \text{Ga–O} \) charge transition at distorted octahedral sites with oxygen vacancies\(^{14}\). In our study, the UV emission has stronger intensity when the film is prepared at a higher oxygen pressure, which means fewer oxygen vacancies. Moreover, Ga ions occupy the octahedrally and tetrahedrally coordinated sites simultaneously in the LGS crystal. So, we assume that the origin of the UV emission does not arise from the distorted octahedral sites, but from the \( \text{Ga–O} \) transition at tetrahedral sites. In order to estimate the contribution of each individual component, deconvolution of the PL spectra (Fig. 3(b–d)) was performed using the Gauss Amp function. The PL profiles are better adjusted by the addition of two peaks after deconvolution. The blue emission appears to account for an increasing proportion of PL intensity with increasing oxygen pressure. This may be attributed to Ga ions occupying more octahedrally coordinated sites at higher pressures. Clearly, the structure merits further investigation.

Fig. 2 AFM images of the LGS films grown at different oxygen pressures
(a) 5 Pa; (b) 10 Pa; (c) 20 Pa; (d) SEM top-view and cross-section (inset) images of LGS thin film prepared at 20 Pa

Fig. 3 (a) PL spectra of the LGS films (\( \lambda_{\text{ex}} = 260 \text{ nm} \)) deposited at different oxygen pressures; peak fitting of the PL spectra of the LGS film deposited at 5 Pa (b), 10 Pa (c), and 20 Pa (d)
3 Conclusions

LGS thin films were deposited on Si (100) substrates by pulsed laser deposition. The films had good preferential orientation along the (220) and (300) orientations, and the intensity of the two diffraction peaks increased with increase in oxygen pressure. The PL spectra of the LGS thin films exhibited a broad emission band ranging from 300 to 500 nm under 260 nm excitation. The emission band split into two peaks (centered at 370 and 432 nm) when the film was grown at 20 Pa. The UV emission was assumed to originate from the Ga–O charge transition in the tetrahedral groups, whereas the blue emission was related to the Ga–O octahedron. The intensity of the PL emission was directly proportional to the oxygen pressure.

Acknowledgments: The authors thank Professor Robert I. Boughton for the detailed revision of this manuscript. The financial aid of the opening project of the MOE Key Laboratory of Mechanical Manufacture and Automation of Zhejiang University of Technology under grant number AMT200506-005 is gratefully acknowledged.

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