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The effect of annealing time on r.f. magnetron sputtered $La_3Ga_5SiO_{14}$ films

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Abstract $La_3Ga_5SiO_{14}$ (LGS) thin films have been grown by r.f. sputtering at 600 °C on (200)-textured MgO buffer layers deposited also by r.f. sputtering on Si substrates. The evolution of crystalline phases in the thin films as a function of time was examined by X-ray diffraction and scanning electron microscopy before and after annealing in air for various times. The morphology of the crystals formed and their formation mechanism were discussed.

Introduction

In the past few years, new piezoelectric material, $La_3Ga_5SiO_{14}$ (LGS), has been extensively studied because of its excellent piezoelectric properties and giant practical values for application in surface acoustic wave (SAW) and bulk acoustic wave (BAW) technologies [1–4]. LGS combines the best acoustic properties of high electromechanical coupling and very low temperature dependence of frequency [5, 6], and therefore allows the development of miniature new generation communication and sensor devices [7, 8].

LGS single crystal has been grown via the Czochralski technique [1–6] although it's congruency region is small [9]. On the other hand, LGS-type crystals and films has been obtained using liquid phase epitaxy (LPE) method [10–14]. However, the simplification of film preparing is necessary in the modern IC fabricating processes. Therefore, the sputtering method seems to be the promising processes to obtain high quality films and it is much simple by comparing with a LPE.

In the present work, LGS films were obtained on MgO layer by a facing target RF-magnetron sputtering system using sintered LGS as target. The MgO layer was used as the diffusion barrier to avoid the silicon diffusing from the silicon substrate. The diffusion of silicon from the substrate into the LGS films would cause the nonstoichiometric in composition in annealing process. In our previous report [15], we found that the as-deposited LGS films are amorphous and have a strong relation to the annealing temperature. In addition, the effect of annealing time on crystallization should be an important parameter. To understand the relationship between the annealing time and the crystallization behavior of LGS film, the characteristics of LGS films annealed with different time are investigated.

Experimental

First, the Si substrates were ultrasonically cleaned by standard process to remove the SiO_2 layer. Then, the MgO buffer layers were deposited by RF sputtering technique with the substrate temperature at 600 °C and a pressure of 2.44 Pa. Annealing followed at 1,000 °C for 24 min.

The 2-inches LGS targets of stoichiometric composition were prepared by conventional ceramics technique, and sintering at 1,400 °C for 10 h. The LGS films were prepared on the MgO/Si substrates by RF sputtering. After the vacuum chamber was evacuated to 3×10^{-4} Pa, Ar gas was introduced into the chamber and the working pressure was kept at 0.8 Pa during the sputtering process. The RF power was 100 W, the substrate temperature was

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600 °C and the sputtering time was 1 h. Then the as-deposited films were annealed at 1,200 °C in air with different annealing times.

The phases contained in the film were examined by 1° grazing angle scan mode using XRD (MAC Sience, M21X) CuK_{α} radiation with 40 kV and 200 mA. The microstructure and chemical composition of the films were analyzed using SEM/EDX (JOEL5600).

Results and discussion

Figure 1 shows SEM photographs of the fractured cross-section of the as-deposited LGS film and the film annealed at 1,200 °C for 5 h. The thickness of the LGS film is about 600 nm and MgO layer is about 300 nm. From the photograph, the surface of the as-deposited film is smooth and the LGS/MgO/Si multi-layer shows good adhesion (Fig. 1a). The surface of the film became rougher with crystalline facets after annealed as seen in Fig. 1b. The LGS film is so intimated to the MgO layer that it is hard to distinguish the interface between the LGS film and MgO layer.

Figure 2 shows (a) the X-ray $\theta/2\theta$ coupling and (b) the 1° grazing scan diffraction patterns of the as-deposited LGS/MgO/Si multi-layer film. Only the (002) diffraction peak of MgO phase was observed from the diffraction pattern in Fig. 2a and no diffraction peak was found in Fig. 2b. This indicates the as-deposited LGS films on MgO/Si are amorphous. Therefore, the annealing treatment is necessary for LGS film crystallization. In our previous report [15], the as-deposited LGS films could be crystallized at 1,200 °C and showed the (110) preferred orientation at 1,250 °C for 5 h. Here, the study on the behavior of phase formation for the LGS films on MgO buffer layer was conducted by change the annealing time.

Figure 3 shows XRD diffraction patterns of LGS films annealed at 1,200 °C under different annealing times. When the as-deposited films were annealed at 1,200 °C for 1 h (Fig. 3a), diffraction peaks were found at $2\theta = 23.9°$, and $2\theta = 29.0°$, 30.8°, and 36.1°. They were identified as Ga_2O_3 and $La_2Si_2O_7$, respectively. No LGS diffraction peak was found for this the annealing treatment. It has been reported that LGS does not undergo phase transformation up to the melting temperature of 1,470 °C [2]. This indicates that the energy barrier for the formation of LGS crystals is very high. Therefore, the formation of Ga_2O_3 and $La_2Si_2O_7$ is ascribed to the crystallization with lower energy barrier than LGS crystals.

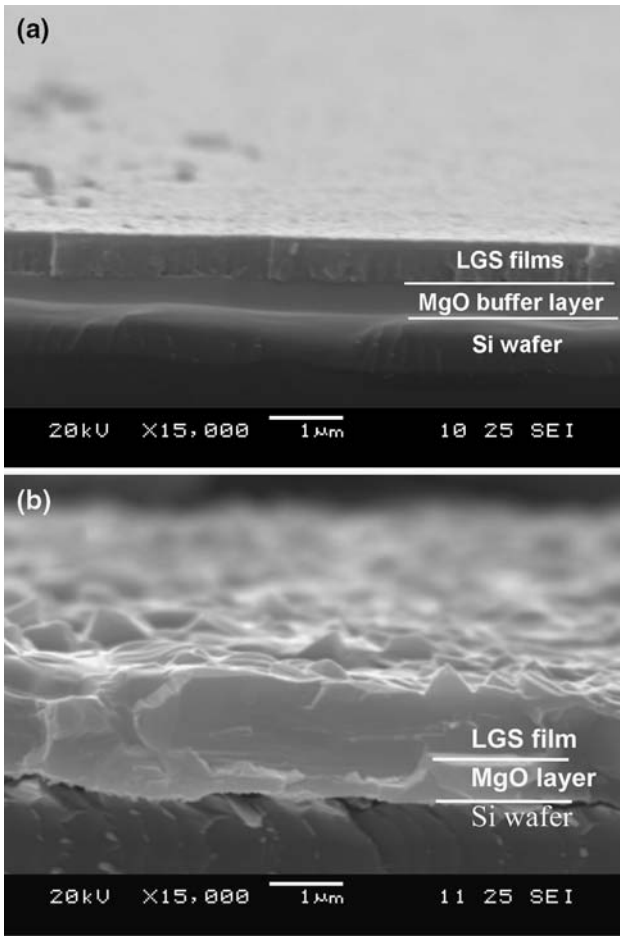

Fig. 1 SEM photographs of the fractured cross-section of the LGS films: (**a**) as-deposited; (**b**) annealed at 1,200 °C for 5 h

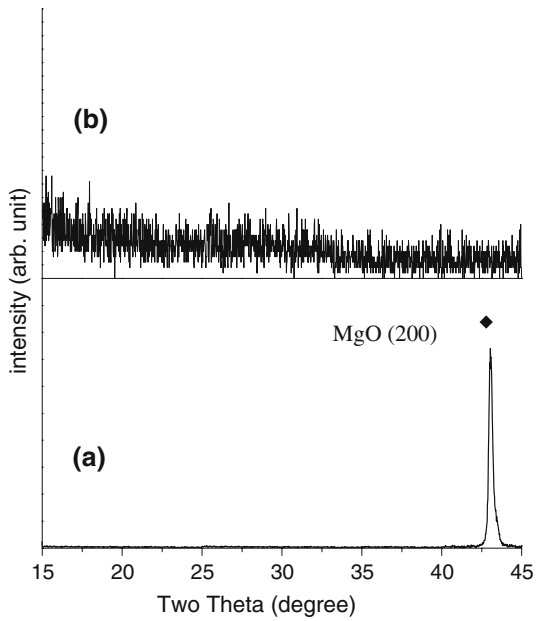

Fig. 2 XRD patterns of the as-deposited LGS films: (**a**) $\theta/2\theta$ coupling scan; (b) 1° grazing scan. ◆: (002) plane of MgO crystal

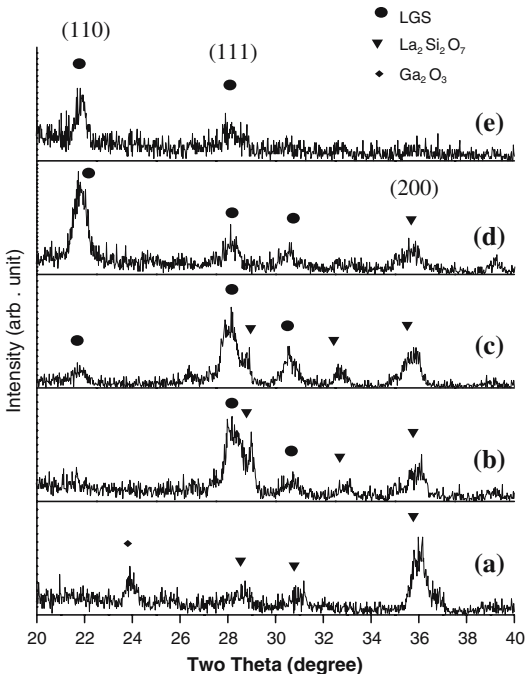

Fig. 3 XRD patterns of the thin films versus various annealing time at 1,200 °C under 1° grazing scan. (**a**) 1 h, (**b**) 2 h, (**c**) 3 h, (**d**) 5 h, and (**e**) 7 h

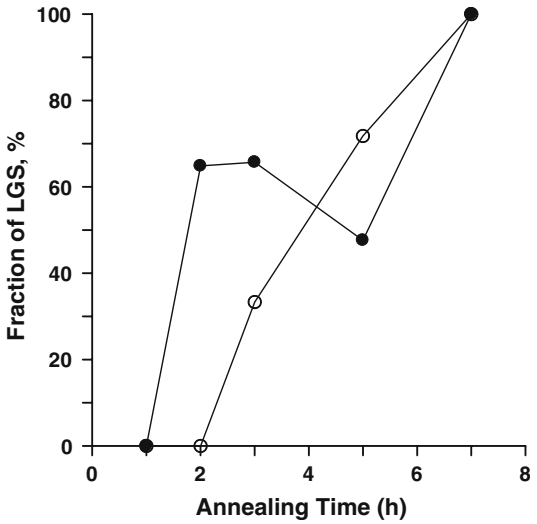

Fig. 4 Relative amount of LGS phase obtained from Eq. (1) versus the annealing time. ●: from the (111) plane, ◯: from the (110) plane of LGS phase

Crystalline phases of LGS and $La_2Si_2O_7$ were observed when the annealing time of the film was increased, as shown in Fig. 3b–d. The new diffraction peaks at $2\theta = 28.0°$ and 30.6° in Fig. 3b were identified as LGS (111) and (201), respectively. The volume fraction of Ga_2O_3 and $La_2Si_2O_7$ decreased when the annealing time was increased. These results are similar to those obtained by Jung and Auh [16] on LGS powder synthesized at lower temperature. In our work, a new peak at $2\theta = 21.7°$ appeared when the annealing time was increased as can be seen in Fig. 3c. The new diffraction peak was identified as LGS (110). The relative intensity of the XRD diffraction peak of LGS (110) increased whereas that of the other LGS planes and $La_2Si_2O_7$ phase decreased as the annealed time increased, as can be seen in Fig. 3d and e.

The percentage of formed LGS phase was calculated by the following equation:

$$\%\text{LGS} = \frac{I_{\text{LGS}}}{I_{\text{LGS}} + I_{\text{LS}}} \times 100\% \quad (1)$$

where I_{LGS} represents the intensity of (111) or (110) reflections of LGS trigonal phase and I_{LS} is for the (200) reflection of $La_2Si_2O_7$ at $2\theta = 36.0°$. The relative amount of the LGS phase calculated from Eq. (1) versus the annealed time is shown in Fig. 4. It was found that the volume fraction of LGS phase steadily increased as the annealing time increased. The (110) diffraction peak of LGS film became apparently with the increase of annealing time. In general, films of covalent compounds would like to grow along the low-index plane to minimize the surface free energy [17]. In equilibrium state, the films grow with the plane of the lowest surface free energy parallel to the surface. Comparing the LGS (111) and (201), (110) belongs to the lower-index plane. Therefore, it is the most stable among the 3 planes considered. When the as-deposited films were annealed especially at 1,200 °C for 7 h, secondary phases were not detected by XRD, as shown in Fig. 3e. This indicated that the secondary phases continued to react and the closed-packed plane transformed into the more stable plane with the increasing annealing time.

The surface morphologies of the LGS films deposited on MgO/Si and annealed for different times are shown in Fig. 5. In Fig. 5a, many fine particles were found on the surface as 1,200 °C/1 h annealing. According to the XRD pattern of Fig. 3a, these fine and island-like particles should be $La_2Si_2O_7$ and Ga_2O_3. The films annealed at 1,200 °C/3 h showed fine grains (~0.1 μm) dispersed in larger grains (~0.8 μm) matrix in Fig. 5b. These fine grains are $La_2Si_2O_7$ whereas the larger grains are LGS crystals as detected from XRD and SEM/EDX analysis. The LGS grains grew very fast and showed the bar shape as the annealing time further increased as seen in Fig. 5c. The bar shape grains implies the anisotropic growth rate for LGS crystals. It has been reported that $Na_2CaGe_6O_{14}$ (NCG) in presence of langasite grew fast along the *c*-axis with specific hexagonal cross-section [18]. The preferred orientation of bar shape grains with (110) plane as shown in the XRD patterns indicates that the direction of the fast

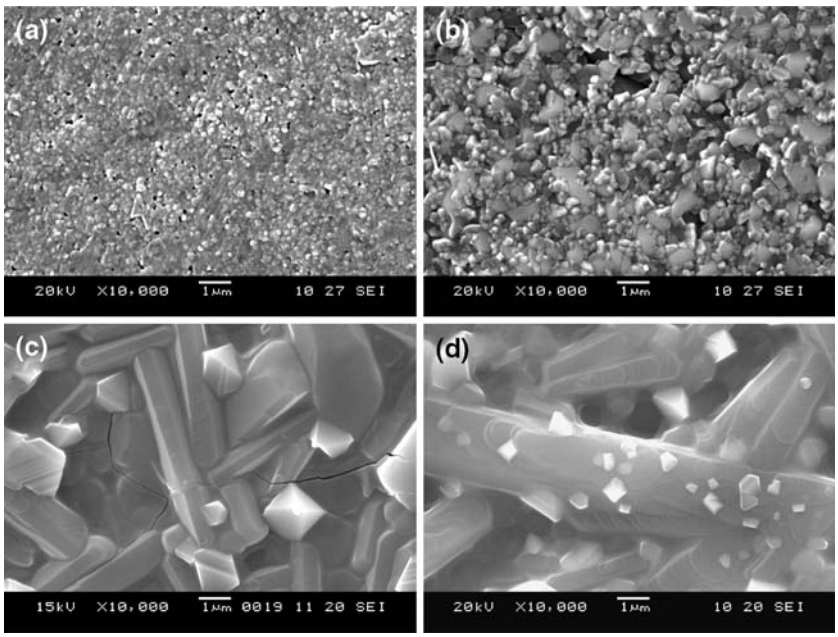

Fig. 5 SEM photographs of the surface of the films annealed at 1,200 °C for (**a**) 1 h, (**b**) 3 h, (**c**) 5 h, and (**d**) 7 h

growing rate might be along the c-axis, which is perpendicular to the (110) plane. Although the (001) plane is more stable than (110) plane, some factors may affect the growing direction of the films such as degree of the lattice match between the film and substrate. The residual second phase of $La_2Si_2O_7$ would transfer into LGS phase as small grains with increasing annealing time as seen in Fig. 5d. Therefore, based on the results preferred orientation on (110) plane of LGS can be obtained by the annealing process.

Conclusion

$La_3Ga_5SiO_{14}$ films were prepared on MgO buffer layers deposited on Si substrates by r.f. magnetron sputtering using sintered $La_3Ga_5SiO_{14}$ as target material. The as-deposited films were amorphous but crystallized during annealing at 1,200 °C for 1 h forming $La_2Si_2O_7$ and Ga_2O_3. These phases were found to transform into crystalline LGS after longer annealing times. The LGS grains grew very fast to form bar-shaped crystals elongated in *c*-direction with prominent (110) facets as the annealing time was further increased.

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