XPS Study of Changes in the Chemical Composition of Langasite Crystal Thin Surface Layers during Vacuum Annealing

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Abstract

La$_3$Ga$_5$SiO$_{14}$ langasite (LGS) crystals have been studied before and after 1000–1050°C, 650°C vacuum annealing. XPS studies have shown that the relative intensity of the gallium bands in the survey spectra of the as-annealed LGS crystals at elevated temperatures is one order of magnitude lower compared to the source specimen. To quantify the changes in the chemical composition of the crystal thin surface layers, we have measured depth profiles with Ar$^+$ sputtering. It was shown that crystal surface is depleted of gallium during annealing at elevated temperatures. We suggest a model in which we attribute the changes in the chemical composition of the LGS crystal thin surface layers during vacuum annealing to the formation of the volatile Ga$_2$O oxide. Vacuum annealing of the LGS crystals at 650°C did not cause any significant changes in the surface chemical composition of the crystals.

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1. Introduction

Oxide crystals of the La$_3$Ga$_5$SiO$_{14}$ composition, or langasites (LGS), are piezoelectric materials. The use of langasite crystals as piezoelectric substrates in wireless surface acoustic wave sensors for measuring pressure and temperature requires high thermal stability of the crystals in vacuum at -196 to 650 °C.

The aim of this work was to study the chemical composition of LGS crystal wafer surface after thermal vacuum annealing at 650°C and at elevated temperatures (1000°C). To analyze the surface and

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subsurface layer chemical composition we used X-ray photoelectron spectroscopy (XPS) depth profiling, and studied crystal bulk chemical composition by X-ray fluorescence (XRF).

2. Experimental

LGS wafer specimens were cut out from Cz single crystals grown in a 2 % argon atmosphere. The wafers were 500 μm thick. Vacuum annealing experiments were carried out at 1000, 1050 and 650°C at residual gas pressures of within 8×10⁻³ for 30 min and 5h.

XPS analysis was carried out on a PHI5500 ESCA spectrometer. Photoemission was excited using nonmonochromatic AL Kα radiation (hν = 1486.6 eV). Depth profiling was carried with 2×2 mm² beam of 2 keV Ar⁺ ions. We interchanged the ion etching and spectrum recording cycles: 3 min etching, then recording the O1s, Ga2p3, La3d and Si2s spectra. Etching rate was determined from etching time and ion beam crater depth. As the crater was not rectangular, the etching rate assessment was approximate, about 2-3 nm/min.

XRF analysis was carried out on an EDAX EAGLE III instrument. We recorded the intensities of the GaKα and LaLα lines for which the escape depth of 90% of fluorescence is 65 μm and 10 μm, respectively, the analysis area diameter being 50 μm.

3. Results and discussion

The 1050°C, 30 min, and 1000 °C, 5 h annealing experiments showed that in both cases the crystals lost color, and the chemical composition of the wafer surface changed: the gallium concentration decreased abruptly. Figure 1 shows the photoelectron spectra of the crystal surfaces before and after annealing from which the gallium line intensity can be seen to decrease by an order of magnitude.

![Survey spectra LGS](image)

Fig. 1. Survey spectra LGS: (a) source LGS, (b) LGS after 30 min annealing at 1050 °C.

These results describe the change in the composition of the top subsurface layers: the mean photoelectron free path is 0.9 nm for the Ga2p3 line and 1.3 nm for the La3d5 line.
Depth profiling showed that the intensity of the gallium lines in the as-annealed specimens is the higher the longer the etching time. To eliminate the error caused by the difference in the sputtering ratios we introduced the quantitative parameters $K/K_0$ showing the factor by which the molar ratio of gallium to lanthanum changed:

$$K = \frac{I(Ga2p3)}{I(La3d)}$$

where $I(Ga2p3)$, $I(La3d)$ are the integral intensities of the Ga2p3 and La3d respectively, and $K_0$ is the $K$ parameters for the initial crystal.

Depth profiling results (the $K/K_0(t)$ curve, Fig. 2) showed that as one moves towards the crystal bulk the molar fraction of gallium increased and tended towards its value for the initial crystal, but even in 60 min of etching which corresponds to 120 – 180 nm the gallium content was 20 % lower than the initial one, see the $K/K_0=1$ curve.

![Fig. 2. Change in $K/K_0$ during Ar+ ion etching: (x) and (o) LGS after 30 min and 5 h annealing, respectively.](image)

XRF analysis also confirmed the large depth of the changes: the GaKα and LaLα line intensity ratio in the specimen after 5 h annealing was 0.98±0.02 of the initial one, i.e. the 10-60 μm thick wafer subsurface layer lost up to 2 % of its initial gallium content.

These changes can be accounted for by the formation of gallium suboxide Ga₂O. During vacuum annealing, thermally induced oxygen desorption increases the concentration of oxygen vacancies, the gallium valence reduces to one, and a volatile Ga₂O phase forms. Similar results for thermal removal of gallium from Ga₂O₃ were reported elsewhere [1], but in the other reducing environment - Ar–6% H₂.

The 650 °C vacuum annealing experiment was carried out for crystals having two orientations, i.e. Z and Y. Analysis of the survey spectra of the Y and Z orientation specimens after 650°C annealing did not reveal any visible changes in the as-annealed chemical composition. However, depth profiling showed that there were slight differences in $K/K_0$ of the two specimens (Fig. 3). To calculate $K/K_0$ for these specimens, we used the average $K_0$ values for several initial specimens having different orientations. $K_0$ deviation from the average value did not exceed 10 %.

The scatter of $K/K_0$ for the Y-orientation specimen has a statistical nature and is within the measurement error. The points of the $K/K_0$ curve for the Z-orientation specimen are below the $K/K_0=1$ curve.
straight curve and do not cross it in 30 min of etching. This suggests that annealing slightly reduced the molar fraction of gallium on the surface of the Z-orientation specimen.

![Graph showing change in K/Ko during Ar+ ion etching of LGS after 5 h annealing at 650°C](image)

**Fig. 3.** Change in $K/K_0$ during Ar+ ion etching of LGS after 5 h annealing at 650°C: (•) Z and (△) Z and Y orientation, respectively.

4. Conclusions

XPS and XRF showed that high temperature vacuum annealing of LGS specimens at 1000–1050°C significantly reduced the molar fraction of gallium near the surfaces of the crystal wafers. The surface gallium concentration decreased 10-fold. The changes in the chemical composition of LGS spread into the crystal bulk, to a depth of more than 100 nm in the subsurface region. We attribute the observed vacuum etching of the LGS crystals to the formation of volatile Ga₂O oxide.

Vacuum annealing of the LGS crystals at 650 °C did not cause any significant changes in the surface chemical composition of the crystals. The surface gallium concentration of one of the test specimens (the Z-orientation specimen) decreased slightly. No changes in the chemical composition of the Y-orientation specimen were observed.

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