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Stability of langasite regarding SAW applications above 800°C in air atmosphere

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Abstract— Y-cut langasite (LGS) crystals are annealed under air atmosphere at temperatures from 800°C to 1200°C, and for time periods between one week and one month. Surface modifications are tracked with energy-dispersive X-ray spectroscopy, secondary ion mass spectroscopy, scanning electron microscopy and atomic force microscopy. This study shows that LGS is suitable for surface acoustic wave (SAW) one-week applications in air atmosphere at temperatures up to 1100°C. Above this temperature, many rough Ga-depleted flaws appear on crystal surface. If application is extended to one month, the maximum operating temperature decreases to temperatures below 1000°C. Indeed one-month annealing at 1000°C causes the apparition of many defects at the surface of LGS crystal. This deterioration impacts the performance of SAW delay lines, increasing insertion losses of 4-5 dB. Moreover, a shift of the operating frequency is also observed, enlarging with the harmonic rank.

Keywords—langasite; high-temperature; SAW; annealing; air

I. INTRODUCTION

In the last fifteen years, surface acoustic waves (SAW) devices have received much attention regarding the possibility of making wireless sensors working in high temperature conditions (above 300°C) using this technology. Indeed, SAW devices are passive components requiring no embedded electronics or power source for wireless interrogation [1]. The choice of the constitutive materials is obviously critical regarding the fabrication of such sensors. Concerning piezoelectric substrate, langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$ or LGS) is currently known as the most appropriate candidate. In fact, it has been intensively studied, demonstrating a good stability at high temperatures, while being commercially available. In particular, Aubert *et al.* recorded a SAW signal on LGS at a maximum temperature of 1140°C for a short-time period [2]. Another remarkable result was obtained by Peirera da Cunha *et al.* who successfully operated LGS-based SAW devices for more than 5½ months at 800°C [3]. However, such performance is conditioned by the environment in which is placed LGS. More precisely, as LGS is an oxide, it is sensitive to oxygen losses, accompanied by gallium ones, depending on oxygen partial pressure and temperature [4]. Thus, several studies evidenced such chemical degradation under slight

vacuum conditions [2], [5]-[6]. Consequently, LGS is particularly suited for high-temperature SAW applications conducted in air atmosphere. Still, one question remains: can LGS really be used in such environment up to 1473°C, which is its melting temperature, as mentioned in numerous papers? Indeed, Fritze demonstrated that LGS-based resonators exhibit piezoelectrically excited bulk acoustic waves at temperatures of up to at least 1400°C [7]. However, SAW applications are much more demanding in terms of stability, as only the very first micrometers under LGS surface (depending on the penetration depth of the waves) are used. Therefore, this area, which is the most exposed to external environment and thus to any degradation effect, has to be stable when exposed to high temperatures, in terms of topography and chemical composition.

This study aims at clarifying the limitations of LGS regarding high-temperature SAW applications in air atmosphere, in terms of material degradation effects.

II. EXPERIMENTAL

Y-cut LGS dies (Witcore Company, Jinan, China) were annealed in static air environment at temperatures from 800°C to 1200°C for one week. Changes in the surface chemical composition were then tracked by energy-dispersive X-ray spectroscopy (EDXS, Tescan Vega 2) and secondary ion mass spectroscopy (SIMS, Cameca IMS 7F). The surface morphology was examined by scanning electron microscopy (SEM, Tescan Vega 2) and atomic force microscopy (AFM, Veeco CP Research). Based on the results, additional LGS dies were annealed at 1000°C for one month and characterized using the above-mentioned methods. SAW measurements were performed at room temperature on delay lines built either from reference (non-annealed) substrates and those annealed one month at 1000°C. Interdigital transducers (IDTs) were made by conventional photolithography and chemical etching from 100 nm thick aluminium films deposited by sputtering method. The devices were composed of two identical IDTs, with 50 pairs of fingers and a wavelength λ fixed to 28 μm . The IDT center spacing, acoustic aperture, and finger width to space ratio were 80λ , 40λ , and 1:2, respectively. The SAW propagation path was along X-direction of LGS.

III. RESULTS AND DISCUSSION

A. Samples annealed for one week up to 1100°C

None of the samples annealed for one week at 800°C, 900°C, 1000°C or 1100°C showed any significant surface change regarding SAW applications. Surface roughness remained so low that getting detailed SEM images was not possible with these samples, just like with the reference ones. Therefore, we accessed the topography of the surface with AFM. All annealed samples up to 1100°C showed identical surface nanostructure, consisting in nanoripples (Fig. 1). The latter hardly changed quantitative values of surface rms roughness, which moved from 3 nm (reference crystals, Fig. 2) to 5-7 nm.

Regarding surface chemical composition, EDXS did not really evidence any significant change either, as the observed variations in the atomic contents of La, Ga and Si are lower than the method resolution (Fig. 3). This result was fully confirmed by SIMS method as the spectra obtained from the reference crystals or the annealed ones seem identical (Fig. 4). SIMS also brought new information on O element which is not quantitatively measurable by EDXS. As for the other constitutive elements of LGS, O content does not seem modified by annealing, even when it lasts one week at 1100°C.

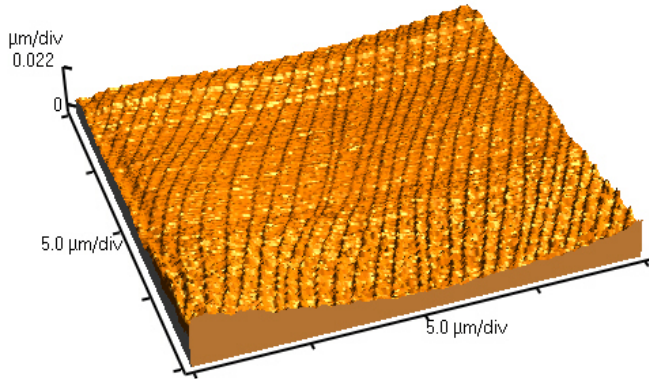


Fig. 1; AFM image of LGS crystal surface after one week at 1100°C under air atmosphere.

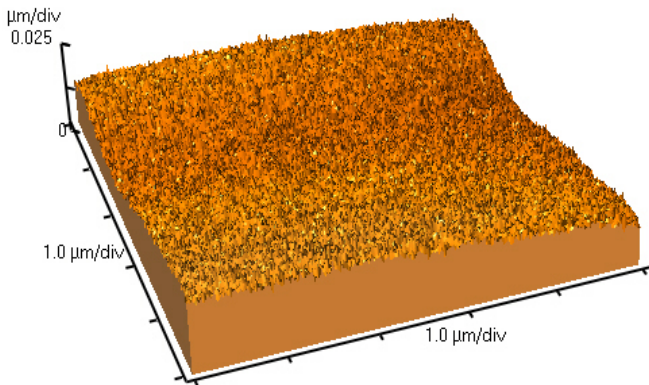


Fig. 2. AFM image of non-annealed LGS crystal surface.

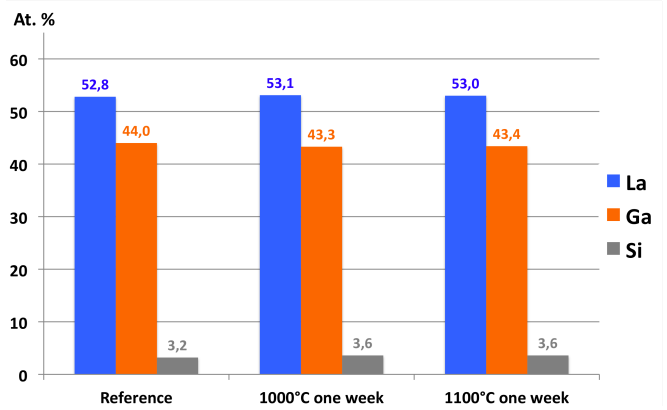


Fig. 3. EDXS chemical composition (atomic percentage) of reference and annealed LGS crystals surface.

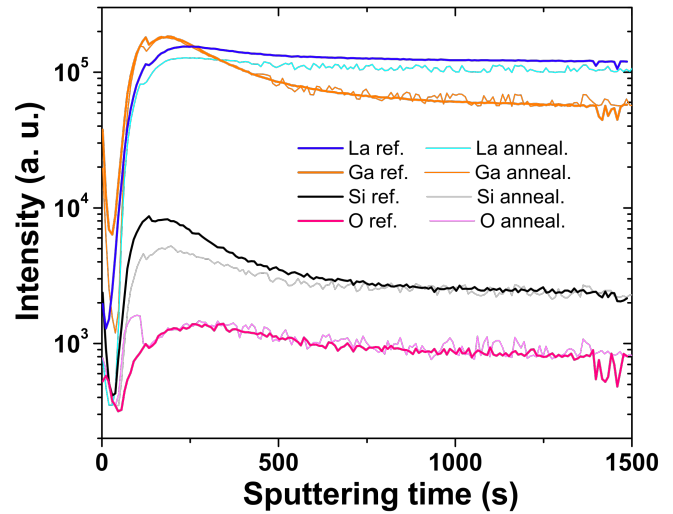


Fig. 4. SIMS depth profiles of reference and one-week annealed at 1100°C LGS crystals

B. Samples annealed for one week at 1200°C

The situation is really different if the one-week annealing is done at 1200°C. In this case, LGS crystal surface becomes really deteriorated, presenting many flaws, which typical diameter is 100 μm (Fig. 5). A more detailed SEM image of one of these defects can be seen on Fig. 6. EDXS reveals that the crystal chemical composition is thoroughly changed in such area, in particular in the center of the spot where Ga content is ten times lower than in the intact regions where the initial composition is practically maintained. Based on these results, coupled to the typical crystal shapes observable on Fig. 7, we assume that a crystallographic phase change, from langasite to some lanthanum-silicon oxide compound, occurred in these areas. However, no determination of the hypothetical new phase has been conducted so far. This chemical deterioration is accompanied by a large increase of surface roughness which reaches 400 nm in the central area of the spots (Fig. 8). Such flaws would surely act as diffraction centers for SAW, and thus significantly degrade the overall response of any SAW device.

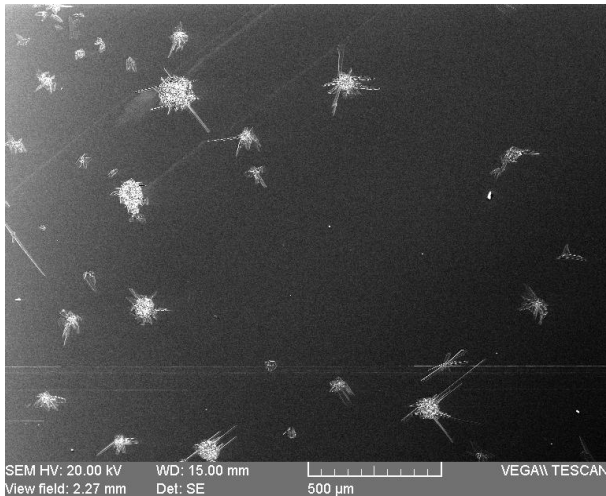


Fig. 5. SEM image of LGS crystal surface after one week at 1200°C in air.

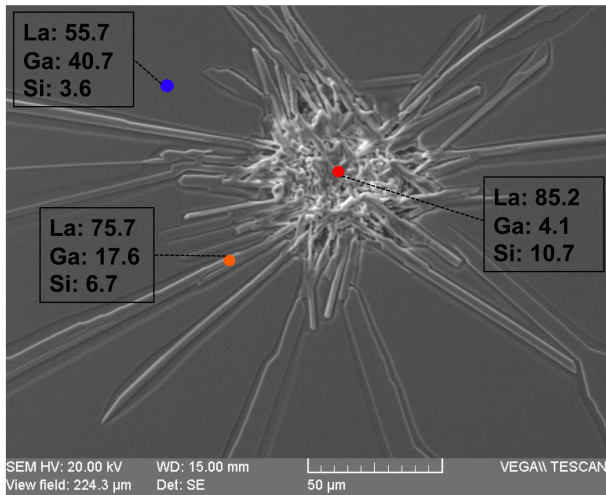


Fig. 6. SEM image of a typical flaw observable on the surface of LGS crystals annealed for one week at 1200°C in air atmosphere. Chemical composition (atomic percentage) measured by EDXS at 3 different points are indicated.

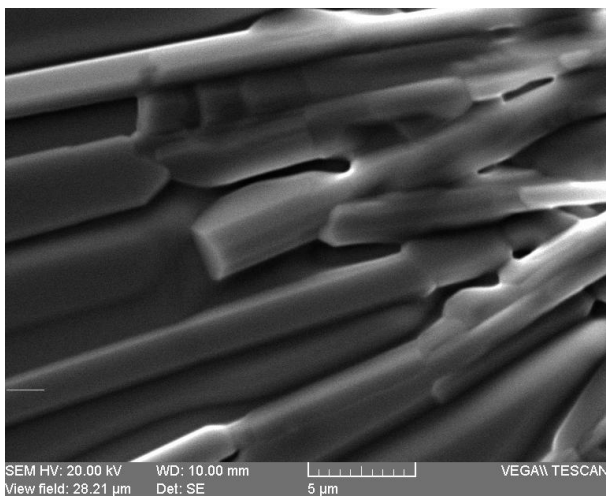


Fig. 7. A more detailed SEM image of the central part of the defect visible on Fig. 6.

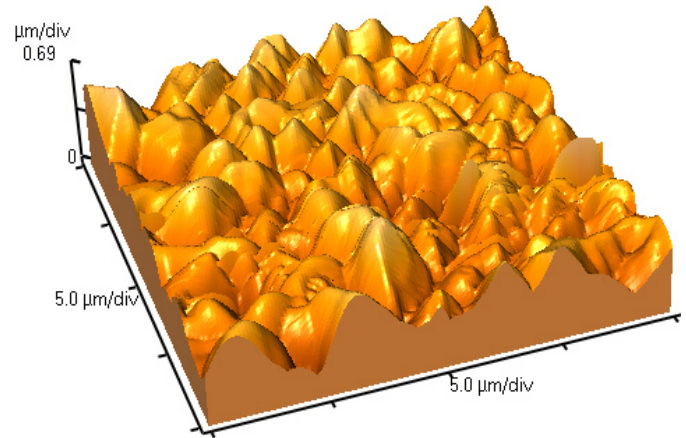


Fig. 8. AFM image of the central part of the defect visible on Fig. 6.

Thus, after these series of one-week annealing, we can conclude that LGS seems stable up to 1100°C regarding SAW applications in air atmosphere for such time period.

In order to get an idea of the limitations of LGS for longer applications, we then made series of one-month annealing. Assuming that in that case, the maximum temperature of stability is lower than 1100°C, the annealing temperature was fixed at 1000°C. This temperature was also obviously chosen because of the psychological threshold it constitutes.

C. Samples annealed for one month at 1000°C

After one-month annealing at 1000°C, LGS crystal surface presents many defects, just like after one-week annealing at 1200°C. Nevertheless, in the present case, these flaws are really in greater numbers, but with a significant smaller size (Fig. 9). Moreover, some differences can also be observed concerning the nature of the defects, when comparing both series of annealing. Thus, if the in-plane spots depicted on Fig. 6 are visible on Fig. 10 as well, one can also observe on the latter numerous out-of-plane defects, which seem to have a chemical composition close to LGS one. This could let think that they are the result of some kind of recrystallization process.

In order to estimate the impact of such alteration of LGS crystals on SAW devices performance, identical delay lines were made either on reference dies and those annealed at 1000°C for one month. These devices were characterized at room temperature and the material chosen to make IDTs was aluminium consequently. This modus operandi was decided as high-temperature *in situ* characterization was not desirable for two reasons. First, we did want to separate the contributions of the piezoelectric substrate and the IDTs in any degradation of the SAW devices behavior. Secondly, as far as we know, there is currently no thin-film material capable to withstand annealing at 1000°C under air atmosphere for periods as long as one month.

It was possible to generate SAW signals on both kinds of substrate, up to the 19th harmonic at 1.854 GHz. This annealing process led to an increase of insertion losses, independent from the frequency, of 4-5 dB. It also induced a shift of the operating frequency, which increased regularly with the harmonic rank (Fig. 11).

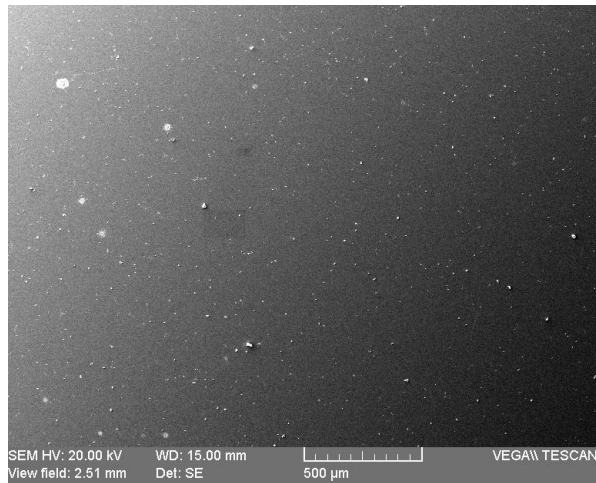


Fig. 9. SEM image of LGS crystal surface after one month at 1000°C in air.

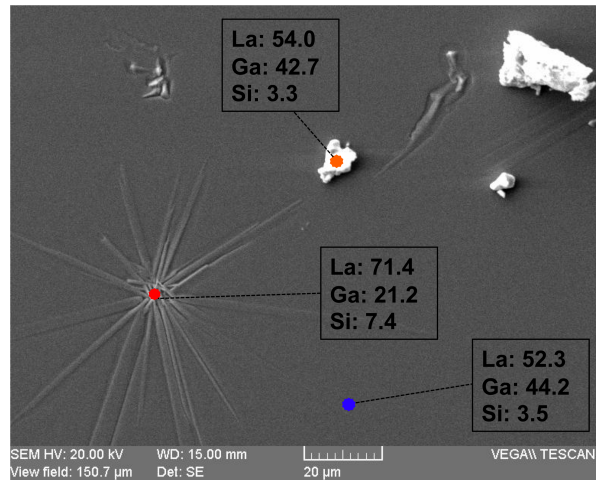


Fig. 10. SEM image of some typical defects observable on LGS crystals annealed for one month at 1000°C in air atmosphere. Chemical composition (atomic percentage) measured by EDXS at 3 different points are indicated.

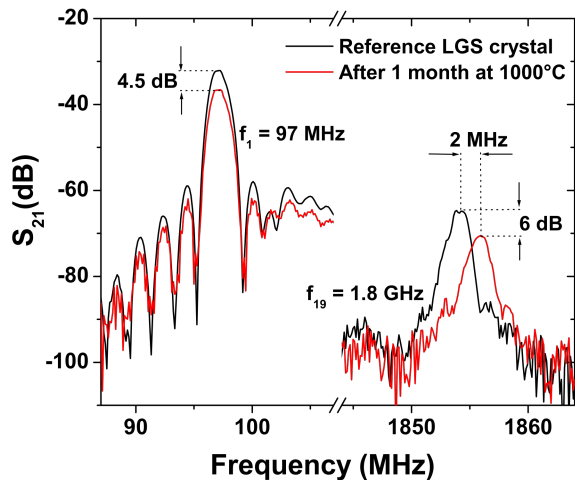


Fig. 11. S_{21} magnitude frequency response (1st and 19th harmonics) of SAW delay lines built from reference and annealed LGS crystals.

IV. CONCLUSION

Y-cut LGS crystals have been annealed in air atmosphere at temperatures between 800°C and 1200°C, for time periods going from one week to one month. Then, the samples were characterized by SEM, AFM, EDXS and SIMS. All four methods revealed that LGS is suitable, from a material point of view, for one-week SAW applications under air atmosphere at temperatures up to 1100°C. If the annealing temperature is increased to 1200°C, numerous defects appear at the surface of the crystal. These defects, which have a typical diameter of 100 µm, are Ga-depleted and show an rms roughness of about 400 nm. Thus, their apparition prevent any use of LGS for SAW purpose at 1200°C, at least for applications as long as one week. If the operating time is extended to one month, the maximum working temperature falls below 1000°C. Indeed, after one month of annealing at 1000°C, many flaws, smaller in size when compared to those described just above, but in greater numbers, were observed at the surface of crystals. These defects caused an increase of 4-5 dB in the insertion losses of SAW delay lines at room temperature, independently from the operating frequency. They also induce a shift of the operating frequency, which increase with the latter, reaching 2 MHz at 1.854 GHz.

Additional experiments are currently conducted to understand the origin of such defects, and to determine the influence of crystal cut on their apparition.

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