NEW MATERIALS FOR MICROELECTRONICS

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1. Introduction

Moscow State Institute of Steel and Alloys (Technological University) has an opportunity on developing and production of new crystalline materials for microelectronics. For these purposes was create OAO Fomos-Materials company. Main attention was dedicated to materials for piezotechnic in particular Lanthanum Gallium Silicate (Langasite) with the chemical formula $La_3Ga_5SiO_{14}$ and Lanthanum Gallium Tantalate (Langatate) with the chemical formula $La_3Ga_{5.5}Ta_{0.5}O_{14.}$

Langasite has been in focus of interest on the part of those manufacturers of surface acoustic wave (SAW) appliances, who are oriented to develop intermediate-frequency filters in the range of 200-400 MHz in the new standard for mobile cellular communication W-CDMA [1]. The physical properties of langasite allow producing thermo-compensated cuts with the zero value of temperature coefficient for the first-order frequency. Among those, the cut near the crystallographic plane (02.2) appears the most promising [2]. Specifics of the Langasite crystal-growing process along the <00.1> axis are studied quite in detail [3]. However, the following cutting of the crystal into slices results in the excessive waste of the material and hence the reduced output and higher cost of the wafers. In order to evade such shortcomings, the langasite crystals must be sown perpendicularly to the axis of growing, like the same is done for the absolute majority of crystals of similar designation.

From another hand Langatate is very interesting material for sensor application. Due to bigger coupling coefficient, higher density, more stable charge dependence vs temperature in the range from RT up to 700 ^oC, big enough resistivity Langatate is unique material for high temperature sensors. The first experiments with sensors using Langatate for combustion chamber in gasoline engine and diesel show very promising results. Given below data are connected mostly to Langasite but the most part of them was used also for Langatate especially in technology process.

2. Preparation of the initial charge

The langasite specific is made by the presence of three basic compounds, such as: oxides of Lanthanum, Gallium and Silicon. In the case of Langatate Silicon oxide was replaced on Tantalum oxide the same purity. These oxides have different temperature dependence of the saturated steams pressure. Because of this circumstance, the mixture of the given oxides may not be used for growing of crystals – especially, large-size crystals – only with preliminary synthesis. In order to produce the synthesized initial mixture we have selected the method of self-spreading high-temperature synthesis (SSHTS), the core essence of which is described [4]. The initial components included lanthanum oxide 99.99 % purity, silicon oxide 99.99 % purity or tantalum oxide 99.99 %, and 5N gallium metallic. The process was realized in two stages, and its fullness was controlled by the X-rays phase analysis method (XRPA). The initial mixture was in composition as stoichiometric. The stoichiometric composition corresponded to the langasite formula, i.e., $La_3Ga_5SiO_{14}$ or langatate formula $La_3Ga_{5.5}Ta_{0.5}O_{14}$. The end product had the form of bricks with the value of density close to that of crystals. Studies of the produced mixture by the XRPA method showed the presence of the basic-phase Langasite or Langatate at the level of at least 90% mass.

III. Cristal grows process

The Langasite-Langatate crystal-growing process was based on the Czochralski method with the HF-heating of crucible, and Iridium was selected as the crucible material. To use platinum and platinum-rhodium alloy would not be appropriate, because at the crystalline melting temper-

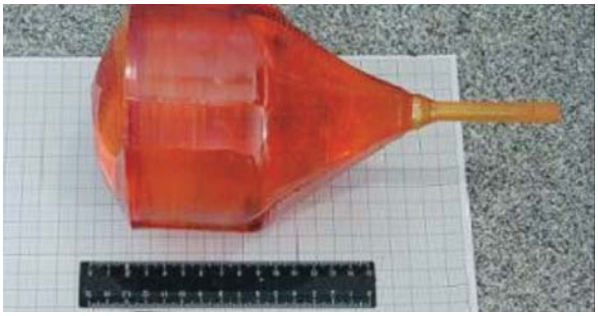

Fig. II.7-1 Typical 120 mm in diameter Langasite crystal

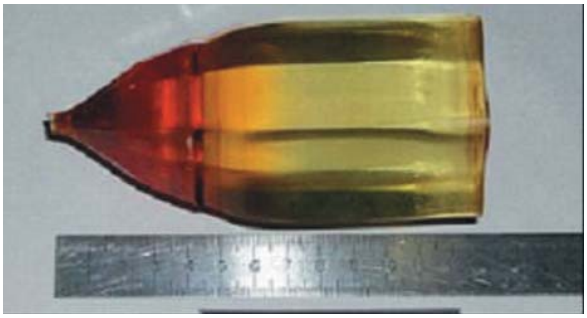

Fig. II.7-2 Typical 65 mm in diameter Langatate crystal

ature these materials have low constructive solidity. The platinum-rhodium alloy with 30% contents of rhodium would attach cherry color to crystals. As shown by chemical analysis, such crystals contain rhodium impurity of 0.05-0.005 % concentration.

The pure argon-based protective atmosphere does not exclude evaporation of gallium oxide from the melt surface, and this factor results in the loss of stoichiometry of the initial composition of the melt. Using the pure argon as a protective atmosphere has a side effect - such as decolorization of crystals and formation of iridium inclusions. The latter inclusions, 10-50 μm in size, are

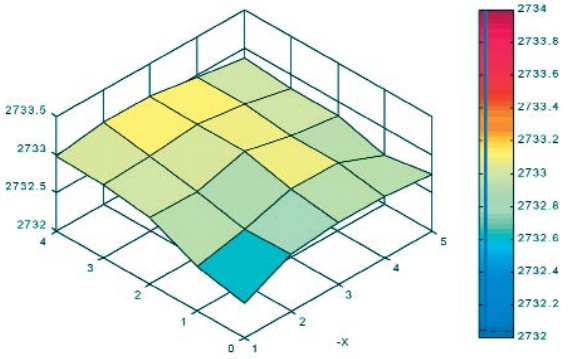

Fig. II.7-3 Average SAW velocity value 2732.73 m/sec standard deviation 0.15 m/sec (56 ppm)

of triangular or hexagonal shape. The initial mixture was melt and crystals were grown in the protective argon atmosphere, with addition of 1-3 vol. % oxygen. The construction of the chamber allows growing of crystals with different values gas pressure. Excessive values of gas-environment pressure under minus 0,2 kgs/cm^2 results in major losses of melted mass through evaporation of volatile components from the free surface even in oxygen content atmosphere. As shown by chemical analysis, the evaporation products consist of gallium oxides. Using of excessive pressure at the mark above + 0,4 kgs/cm^2 is not possible because of construction specifics of the growth chamber.

The seed crystals were oriented along the crystallographic axis <00.1> and <02.2>. The crystal growth speed was 0.5...3 mm/hour, with the seed rotation frequency as 15...40 rpm.

A typical Langasite crystal, grown along the crystallographic axis <02.2>, is shown in Fig. II.7-1. A typical Langatate crystal, grown along crystallographic axis <00.1>, is shown in Fig II.7-2.

4. Method of the saw velosity measurement

Saw quality Langasite wafers must have low velocity deviations within the wafer and equal value of average velocity within the lot of wafers. The upper limit of SAW velocity deviation within the wafers cannot be higher than 150 ppm. A method of non-destructive measurement was create. The acoustic parameters of the wafers - namely, the average value and SAW velocity deviation - have been measured by the methodology, described in [5]. This method is based on measurement of time delay between the two homogeneous interdigital transducers (IDT), positioned at a fixed distance from one another.

The measurement device includes the acoustic system consisting of a sensing element and the piezoelectric wafer under study, as well as the Vector Network Analyzer. The sensing element of the acoustic system is made on the substrate, manufactured from a non-piezoelectric material, with two IDTs with split electrodes, positioned on the surface. The IDTs electrodes period is equal to 13 μm, aperture 4 mm, and distance between the IDTs - 14 mm. The piezoelectric wafer is placed on the system of transducers.

The output signal of the acoustic system is the result of the interference of input and output IDT frequency characteristics. By the acoustic system's complex frequency characteristic, measured by the Vector Network Analyzer, it is possible to identify the impulse characteristic of the acoustic system with the help of Furie-transformation.

The total error (mathematical calculation and influence of the acoustic system) would amount to 35 ppm of the measured velocity value.

Measurements were made for Langasite wafers 100 mm in diameter. As shown by the measurement results, the average value of the SAW velocity corresponds to 2732.73 m/sec, while the standard deviation amounts to 0.15 m/sec or 56 ppм. As shown by the obtained data, the value of the SAW velocity as well as its standard deviation give the possibility of successful usage of Langasite wafers for mass production SAW filters for 200...450 MHz.

By all evidence, the acoustic homogeneity of Langasite crystals is determined to a great extent by other parameters of the growing process - such as chemical composition of the initial mixture, the extent to which the crystal growing conditions deviate from the equilibrium, impurity content etc.

5. High resolution X-ray difraction

Measuring full width at half maximum (FWHM) of rocking curves (crystal rotation around the Bragg angle and fixed detector) is a powerful method allowing the structural quality of the crystal to be characterized. A crystal is usually considered as perfect if the measured rocking curve FWHM is comparable to the theoretical value. Unfortunately, these theoretical values are

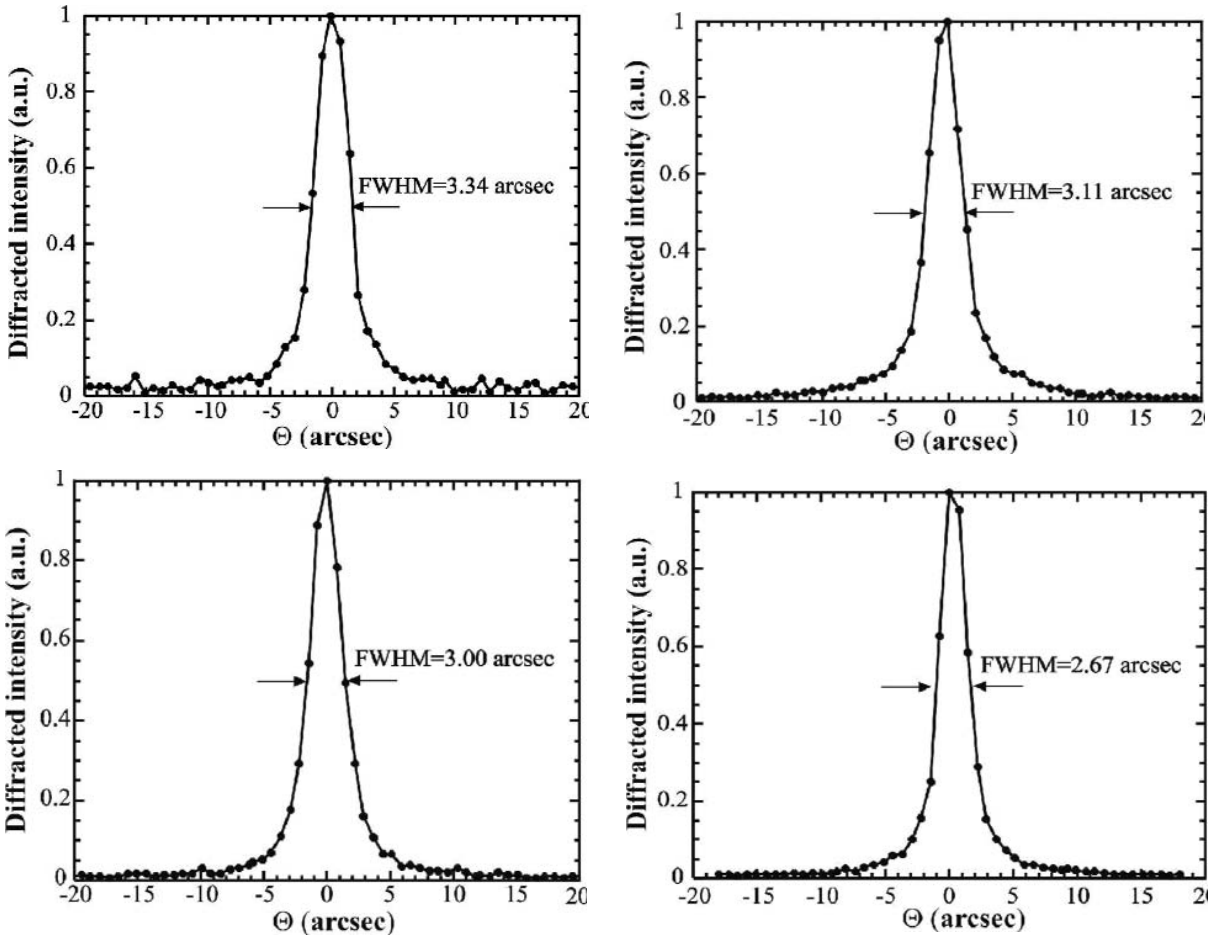

Fig. II.7-4 Experimental rocking curves of Y-cut LGS for a sequence of (100) – (400) reflections.

not yet available for LGS. However, to estimate the crystal quality, the experimental FWHM can be compared with the well-known rocking curve FWHM of perfect silicon crystals (used as monochromator in most X-ray experiments). Figure II.7-4 presents experimental rocking curves of Y-cut LGS for a sequence of (100) – (400) reflections. Their FWHM are FWHM(100) = 3.34 arcsec, FWHM(200) = 3.00 arcsec, FWHM(300) = 3.11 arcsec, and FWHM(400) = 2.67 arcsec. At E = 17.479 keV, the theoretical Si (111) FWHM is FWHM(111) = 4.36 arcsec. This suggests, on the basis of experimental measurements, that this LGS crystal is of very high quality. In this experiment the X-ray beam size was only 10 μm by 10 mm and therefore rocking curves were measured from a small crystal area. To study crystal structure perfection on a larger scale, rocking curves should be measured from many crystal regions.

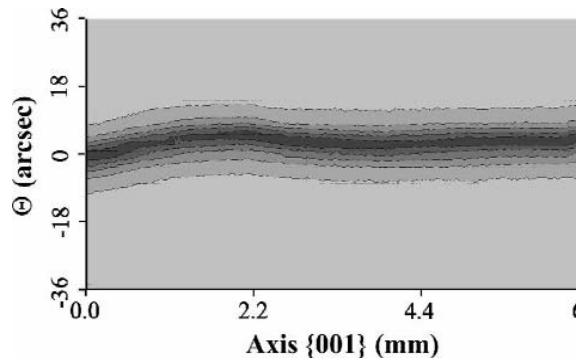

Fig. II.7-5 Map of the diffracted X-ray intensity distribution along the {001} growth axis ((300) reflection)

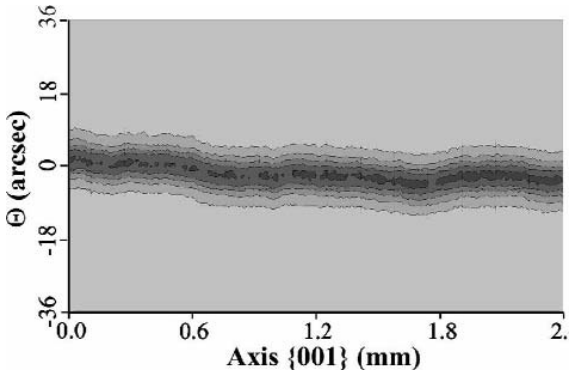

Fig. II.7-6 Map of X-ray diffracted intensity distribution along the {001} crystal growth axis for the (330) reflection.

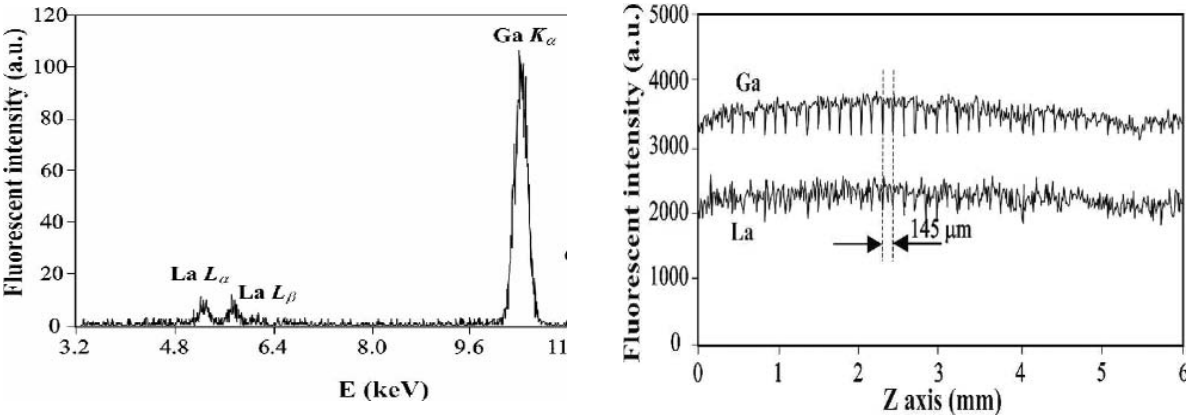

Fig. II.7-6 Map of X-ray diffracted intensity distribution along the {001} crystal growth axis for the (330) reflection.

Figure II.7-5 shows a map of the diffracted X-ray intensity distribution along the {001} growth axis ((300) reflection). Between each of the 661 rocking curves, the crystal was moved by steps of 10 μm. The figure shows that a small change in the diffraction maximum position (Bragg peak position) occurs along the growth axis. This is due to a small variation of the d(300) interplanar spacing along the crystal growth axis. The maximum deviation of the Bragg peak angular position was WM = 2.5 arcsec at the distance 6.6 mm along the crystal growth axis. Using the Bagg law, the interplanar distance deviation can be estimated: Xd(300)/d(300)Y8.10-5. Similar measurements on an X-cut LGS crystal were also made using (110) — (330) reflections. The results are FWHM(110) = 2.66 arcsec, FWHM(220) = 2.44 arcsec, and FWHM(330) = 1.78 arcsec. A map of X-ray diffracted intensity distribution along the {001} crystal growth axis for the (330) reflection is presented in Fig. II.7-6. 241 rocking curves were measured for the map and Xd(330)/d(330)Y9.10^{-5}.

6. X-ray microfkuorescent analysis

X-ray fluorescence analysis was used to study the Ga and La spatial distribution along the growth axis of a X-cut LGS crystal. The footprint of the beam on the crystal surface was decreased to 7x100 μm in order to obtain the best spatial resolution as possible. At E = 17.479 keV (MoKS1), both LaLS (5 keV) and GaKS (10.47 keV) edges are excited. Figure II.7-7 presents fluorescence spectrum of the LGS crystal, measured with a solid state Ge detector positioned parallel to the crystal surface. LaLS and GaKS fluorescence intensities along the crystal growth axis are presented in Fig. II.7-7(b). A periodic modulation (145 μm) is observed and corresponds to the growth banding period. Those results demonstrate that an abrupt synchronous reduction of La and Ga atom concentrations occurs on the boundary between adjacent growth bands.

7. Conclusion

The above described results show high perfection of grown crystals. The batch production of crystals now is organized. Properties and applications in details described in the literature and results of numerous researches show an opportunity of wide use of these materials.

References

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