

THIN FILMS OF LANGASITE ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) PREPARED BY PULSED LASER DEPOSITION

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Thin films of langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$) have been prepared from langasite crystal targets by pulsed laser deposition. The films deposited at room temperature on silicon wafers are amorphous. After annealing at 700 °C, in normal atmosphere, the films crystallize as polycrystalline langasite oriented with the plane (001) parallel to the surface of the silicon substrate.

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1. Introduction

The lanthanum gallo-silicate, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$, or langasite (LGS) is a new material with piezoelectric properties, which is analogous to quartz.

The langasite was obtained for the first time by Kaminski et al. [1]. This group first initiated the research on the structure and properties of langasite crystals.

Dubovik et al. [2] have shown that the functional parameters of the piezoresistive elements are superior to those of quartz: the resonance interval is 2-3 times larger, the inductance and dynamical resistance for the bulk acoustic waves (BAW) are 6-18 times and 2-6 times lower, respectively. The electro-mechanical coupling coefficient is 2-3 times higher and the attenuation for the surface acoustic waves (SAW) are two times lower, while the size of the piezoresistive elements is reduced by 20-30 %, as compared to quartz parameters.

Sacharov et al. [3] produced monolithic filters for GSM, based on langasite, and demonstrated that this new material can be applied to piezoelectric engineering. The most promising field is that of SAW and BAW devices.

The outstanding dielectric properties of langasite make it an important material in microelectronics for ultrathin insulator coatings.

Recently, there were prepared thin langasite films by epitaxy in liquid phase. Zhan et al. [4] have shown that the langasite layers can be grown on spinel substrate (MgAl_2O_4).

The problem of the preparation of thin films of langasite or other compounds from the same family, as e.g. langanite ($\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$) or LGN and langatite ($\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$) or LGT is important to both the material science as well as to applications in VLSI microelectronics.

In this paper we report the results obtained in the research dedicated to the preparation of thin langasite films by laser ablation procedure.

2. Experimental

Langasite crystals were grown by Czochralski method. Starting materials were prepared by mixing 99.99 % pure La_2O_3 , Ga_2O_3 and electronic grade SiO_2 at a composition close to the stoichiometric one (with an excess of gallium). The growth atmosphere was nitrogen with ~10 % oxygen.

Thin langasite films were deposited by pulsed laser deposition (PLD) using a KrF* excimer laser (248 nm wavelength of the emitted UV pulse, pulse duration >20 ns, 1 Hz repetition rate and maximum output energy of 85 mJ/pulse). The pulse was focused on the target through a MgF_2 cylindrical lens. Focal length was of 30 cm. The incidence angle to the target was 45° . The laser spot was set within 4.2 and 6.4 mm^2 and the incident fluency varied roughly in the range 0.8- 1.6 J/cm^2 .

The target material was a platelet cut from a bulk langasite crystal of size $15 \times 15 \times 2 \text{ mm}^3$ grown by Czochralski method in our laboratory, using high purity elements. The holder with the langasite target was placed in stainless vacuum chamber, which was subsequently evacuated down to $1\text{-}7 \times 10^{-3} \text{ Pa}$. The target was rotated with the frequency of 0.4 rot/min during PLD process. The substrate for film deposition was a (100) oriented silicon wafer placed on a molybdenum-heating block, parallel to the target surface and situated at a distance of 2-5 cm. Total number of pulses applied in two stages for the deposition of the film was of 47 000.

The structure of the langasite films has been determined by X ray diffraction. A TUR M62 diffractometer and copper target tube has been used to this purpose. For the amorphous films the X-ray patterns were carefully recorded in the angular interval $8\text{-}74^\circ (\theta)$.

The crystallization of the amorphous films were achieved by heating the samples in an electrical furnace. Heating rate was of $11^\circ\text{C}/\text{min}$. The deposited material was annealed at 700°C for hours. After the heat treatment the sample was cooled down to the room temperature in one hour. The annealing of the films was performed in normal atmosphere.

3. Results

After the application of 47000 subsequent laser pulses, the thickness of the langasite thin films proved to be thick enough for proper investigation by X-ray method.

The as-prepared langasite thin films resulted to be amorphous (Fig. 1). An intense first one and a large and weak second maxima are the most important characteristic of the X-ray patterns.

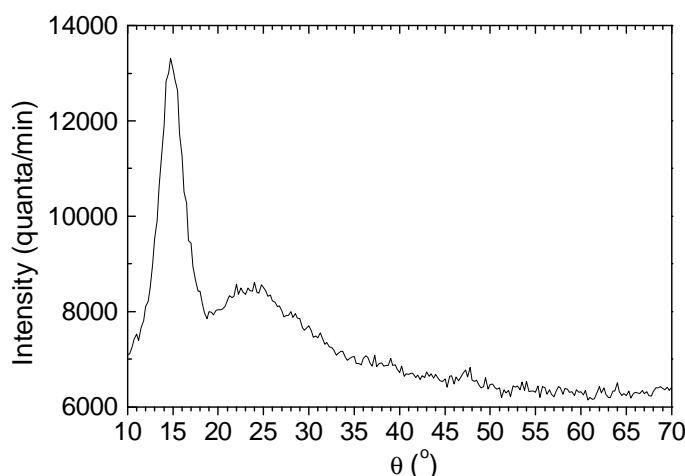


Fig. 1. The X-ray diffraction diagram of thin langasite film prepared by PLD.

In order to calculate the atomo-electronic radial distribution function the incoherently scattered radiation was subtracted. The experimental intensity function was corrected for polarization,

transformed into electronic units and scaled to independently scattering atoms at high diffraction angles. We thus obtained the normalized coherent intensity, $I(k)$. The atomo-electronic radial distribution function (RDF) is defined as:

$$RDF = 4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_{k_{\min}}^{k_{\max}} k \sin kr \left[\frac{I(k)}{f^2(k)} - 1 \right] dk . \quad (1)$$

Here $\rho(r)$ stands for the atomic density at distance r from an arbitrary origin, ρ_0 the average atomic density of sample, $f(k)$ the scattering factor of La₃Ga₅SiO₁₄ corrected for the anomalous dispersion and k the scattering vector ($k = (4\pi \sin\theta)/\lambda$).

The atomo-electronic radial distribution function calculated from the X-ray diffraction pattern is shown in Fig. 2.

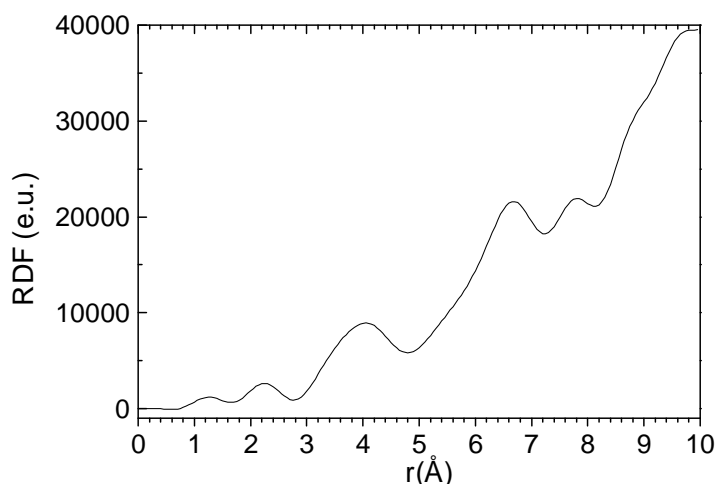


Fig. 2. The radial distribution function of the amorphous langasite film.

The first maximum in atomo-electronic RDF is centered at 2.253 Å, which is close to the mean distance calculated from the bonding distance between lanthanum and oxygen ions (2.50 Å) and that between gallium and oxygen ions (2.09 Å). The ionic radius of La³⁺ in langasite is 1.17 Å and the ionic radius of Ga³⁺ in langasite is 0.76 Å [4], while O²⁻ radius is 1.33 Å. The presence of the first coordination distance typical of langasite crystals speaks in favor of the preservation of the local order in the amorphous state of the material based on langasite composition. Other peaks in RDF are situated at 4.023 Å, 6.677 Å and 7.8 Å. The second neighbour distance in amorphous langasite corresponds to the inter-ionic Ga-La distances, taking into account that these ions occupy different crystallographic sites. From the differential radial distribution function we have obtained the positions of the coordination spheres in the langasite film with an improved accuracy: $d = 2.197$ Å, 3.913 Å, 6.583 Å and 7.693 Å.

After the investigation of the fresh amorphous film by X-ray diffraction, the film has been annealed at 700 °C for 2 hours. The X-ray diffraction pattern recorded on the annealed film is shown in Fig. 3.

Several narrow peaks appearing on the diagram demonstrate the full crystallization of the film. The most part of these peaks can be ascribed to langasite. The anomalous intensities of the (001) and (002) diffraction peaks speak in favor of a strong preferential orientation of the langasite crystallites on the wafer substrate. The normal intensities of these lines can be observed on the Fig. 4, that illustrates the X-ray pattern of a langasite powder prepared from a small chunk of single crystal of langasite.

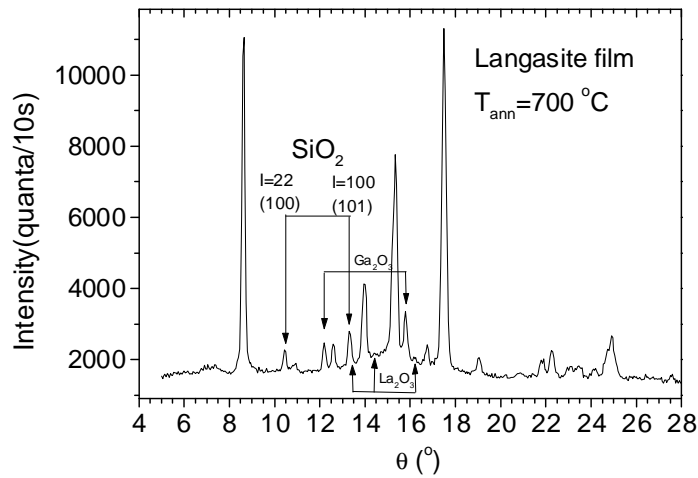


Fig. 3. The X-ray diffraction diagram of the langasite film annealed in ambient atmosphere for 2 hours at 700 °C.

The minor phase present on the diagram of the crystallized langasite film can be attributed the most probably to SiO_2 (low quartz). Other minor phases are Ga_2O_3 (evidenced by the peak at $d = 2.831 \text{ \AA}$ and the large peak situated around $d = 6.0 \text{ \AA}$) and La_2O_3 (evidenced by the small peaks situated at $d = 2.76 \text{ \AA}$ and $d = 3.17 \text{ \AA}$). These oxides result from the decomposition of langasite. The presence of the double oxide LaGaO_3 was not firmly demonstrated.

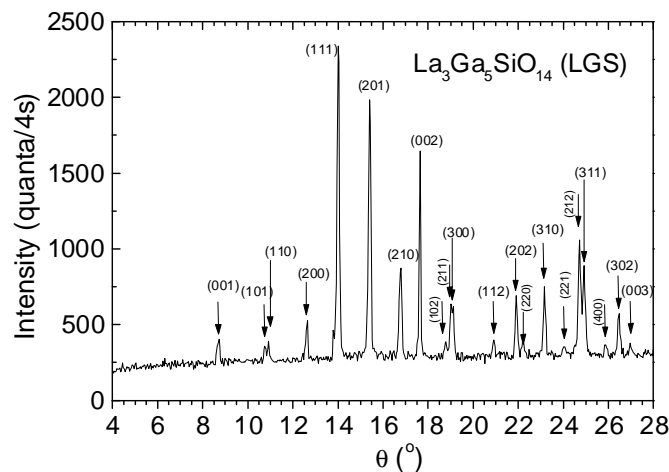


Fig. 4. The X-ray diffraction diagram of langasite powder.

The lattice parameters of the langasite single crystal used in our experiments (space group P321, point symmetry class 32) were determined from the X-ray powder diagram (Fig. 4). They are: $a = 8.159 \text{ \AA}$ and $c = 5.095 \text{ \AA}$. We note that Takeda et al. [5] reported the value $a = 8.1665 \text{ \AA}$, while Bohm et al. [6] published the values: $a = 8.161 \text{ \AA}$ and $c = 5.091 \text{ \AA}$. We calculated the lattice parameters of the langasite phase in polycrystalline film, deposited by PLD, of $a = 8.17 \text{ \AA}$ and $c = 5.13 \text{ \AA}$. The lattice parameters put in evidence a small expansion of the ideal unit cell of langasite. This expansion can be ascribed to the disordered distribution of cations on various types of crystallographic sites. In langasite the cations are distributed over three types of sites: i) decahedral sites coordinated by 8 oxygen atoms, ii) octahedral sites coordinated by 6 oxygen atoms and iii) tetrahedral sites coordinated by 4 oxygen atoms. Lanthanum cations occupy the decahedral sites.

Silicon occupies the tetrahedral sites. Gallium cations are distributed over all types of sites (excepting the dodecahedral ones). Langasite does not form a framework structure as does quartz but rather layered structure of (Ga, Si)O₄ tetrahedra perpendicular to the crystallographic c-axis. The layers are connected by octahedrally coordinated gallium ions and eight-fold coordinated lanthanum ions. The change of position of the cations on different crystallographic sites influences the lattice parameters. This is similar to the case of spinels, where the change from the normal spinel to inverse one is accompanied by a modification of the cubic lattice parameter. The ordered arrangement of the cations is obtained in the ideal crystals only. Some deviation from the langasite crystal stoichiometry can be, also, due to the cause of the difference in the values of the crystal cell parameters. The separation of the minor phases can account for the deviation of the obtained langasite polycrystalline thin films from the stoichiometric composition.

The microstrains and the mean size of the langasite crystallites can be determined simultaneously if one uses the diffraction lines corresponding to two or more orders of diffraction. In the langasite crystallized films the maxima (001) and (002) are intense due to the preferential orientation of the crystallites. Consequently, the integral breadths of the peaks can be determined very accurately. In the limiting case of pure particle size broadening the line breadth β_D is related to the effective (or mean) particle size D , the X-ray wavelength, λ and the Bragg angle, θ , according to the equation:

$$\beta_D = \lambda / (D \cdot \cos\theta) \quad (2)$$

For pure stress broadening the breadth β_η is related to the effective strain η and the Bragg angle, θ , by the equation:

$$\beta_\eta = \eta \tan \theta \quad (3)$$

If both types of broadening are present, the resultant breadth β should be the convolution of the widths. Wood and Rachinger [7] have shown that for a commonly occurring line shape the widths are additive. This means that $\beta = \beta_D + \beta_\eta$. In this case one can write:

$$\beta \cdot \cos\theta / \lambda = 1/D + \eta \cdot (\sin\theta / \lambda) \quad (4)$$

In a distorted lattice the mean particle size, D , is interpreted as a measure of the volume of regions which diffract coherently. In anisotropic materials the strain distribution depends on the type of crystallographic plane and, frequently, the following relationship describes better the experimental breadths:

$$\beta \cos\theta / \lambda = 1/D + (2\eta / E_{hkl}) \cdot (\sin\theta / \lambda) \quad (5)$$

In equation (5) E_{hkl} is the value of the Young modulus for the direction perpendicular to the planes (hkl) and η is the stress distribution function, which is assumed to be independent of direction. The method of simultaneous calculation of the particle size and distortion is similar to that from the paracrystalline theory (where g denotes the paracrystalline distortion fluctuation parameter). The application of the paracrystalline theory to the disordered materials is described in Ref. [8]. In the case of langasite crystallites the mean size of the crystallites, D , perpendicular to the planes (001), and the mean square strain or the width of the (micro) strain distribution, $\eta = \Delta c/c$, can be calculated from the equation (4), based upon two reflections of the same type (e.g. 001 and 002).

The results obtained from calculations are: $D = 600 \text{ \AA}$ for the mean size of the crystallites measured perpendicularly to the (001) planes and $\eta = \Delta c/c = 1.4 \%$ for the strain within the crystallites along the direction of the axis c . The instrumental broadening was established by measuring the profiles of the (001) and (002) diffraction lines of a powder sample of langasite. The mean size of the crystallites and the mean square strain are of the same order of magnitude with those found in other materials, as e.g. in graphite [9]: 530 \AA and 0.12% , and in polyethylene single crystal [10]: 200 \AA and 1.3% .

4. Conclusions

Thin amorphous films of langasite have been successfully prepared by pulsed laser deposition from a single crystal target onto a silicon wafer. The films have been completely crystallized by annealing for two hours at 700 °C. Polycrystalline, highly (001) oriented langasite films have been obtained with the mean size of the crystallites close to 600 Å and (micro)strain value along the axis c of $\Delta c/c = 1.4\%$.

The possibility to get by simple procedure thin crystalline and highly oriented langasite films opens the way to apply these materials in microdevice applications.

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