Defects and acoustic properties of LiAlO$_2$

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A potential piezoelectric crystal LiAlO$_2$ with (100) orientation is grown by means of the Czochralski pulling method. The as-grown crystal is identified as a single phase with good uniformity by x-ray diffraction pattern. (001) Transmission electron microscope image showed a unique cross-hatched pattern which reveals a superlattice structure. Several cubic LiAlO$_2$ specimen, 10.0 mm $\times$ 10.0 mm were manufactured to characterize its elastic properties. The time-based pulse-echo transmission technique was employed to measure the acoustic velocities of longitudinal and transverse modes. The elastic constants of LiAlO$_2$ were extracted from the acoustic velocity measurements at different propagation directions. It was found that the acoustic velocities of LiAlO$_2$ are much higher than the current piezoelectric crystals, including quartz, LiNbO$_3$, and Langasite family materials. © 2006 American Institute of Physics. [DOI: 10.1063/1.2183365]

LiAlO$_2$ crystal belongs to the space group symmetry $P4_{1}2_{1}2$ in which each lithium and aluminum atom is coordinated at the center of tetrahedron, with four oxygen atoms.$^1$ It was found to be piezoelectric by Remeika$^2$ in 1964. Recently, LiAlO$_2$ attracted more attention as a potential substrate for growing III–nitride semiconductors. It has certain unique properties. The lattice mismatch between LiAlO$_2$ and GaN is estimated to be less than 1.4%. Second, after GaN epitaxial growth, LiAlO$_2$ substrate can be removed by chemical etching. The total area for device manufacturing is enlarged. GaN grown on (100) LiAlO$_2$ substrate is along the $M$ plane (10-10), which places the polar $c$ axis in the wafer’s plane. In this orientation, the quantum confined Stark effect which causes a redshift in emission can be eliminated.$^{3-5}$ However, there is a lack of information on its growth defect and acoustical properties in previous reports.

The motivation to do this research is based on scientific curiosity and the possible acoustic applications of LiAlO$_2$. At present, the largest application of the piezoelectric materials is to make surface acoustic wave (SAW) devices as frequency filters in the wireless communication. Commercial crystals are quartz and LiNbO$_3$. Quartz has low acoustic loss and temperature stability, but due to its narrow bandwidth and small piezoelectric constant, it has limitation in the fabrication of certain filters. Quartz is also limited by its tendency to form twin domains under pressure at temperatures above 350 °C. LiNbO$_3$ has a high coupling constant, making it a proper material for acoustic transducers, but the temperature shift is large which is not suitable for band pass filter in wireless communication systems. Since LiAlO$_2$ shows it piezoelectric properties and high acoustic velocities, it might be a potential candidate for these acoustic applications.

In this letter, a single LiAlO$_2$ crystal was grown by the Czochralski pulling technique, and its growth defect was evaluated by using an electron microscope. The measurements of acoustic velocities of longitudinal and transverse modes were done by means of the time-based pulse-echo transmission technique. This approach is found to be efficient and accurate over the frequency interest, and can be fully automated using computer control. The elastic constants of LiAlO$_2$ were then extracted from the acoustic velocities at different propagation directions.

Single LiAlO$_2$ crystal was grown by the Czochralski pulling technique. The starting raw materials of 99.99% purity were prepared from a mixture of Li$_2$CO$_3$ and Al$_2$O$_3$ powders. Since Li$_2$O will volatilize severely during the growth, 5%–10% excess of Li$_2$CO$_3$ in weight fraction was added. The raw materials were then placed in an iridium crucible. An iridium lid was used to seal the crucible to prevent the charge from evaporating, baking them at 1200 °C in order to decompose CO$_2$ and reduce the material’s volume. They are then heated to approximately 1750 °C to melt the materials. In order to reduce the vertical temperature gradient and avoid the crystal decomposition, an upper ZrO$_2$ heat shield was put on the top of the iridium lid, which works as an after heater. Figure 1 is the as-grown (100) LiAlO$_2$ single crystal. The top of the crystal showed an opaque and milky structure which results from the chemical decomposition. The lower part of the crystal has many inclusions precipi-

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FIG. 1. LiAlO$_2$ single crystal with the (100) growth orientation.
tated in it. A green laser was used to evaluate the crystal’s overall quality. The laser beam was scattered slightly by the voids and inclusions. The voids were caused by the high oxygen concentration. When the oxygen concentration continues increasing and reaches its solubility limit, it will diffuse into the crystal and then form the voids. The inclusions result from the nonstoichiometry of the melt. In addition, the crystal surface is not very smooth. This is because the surface was etched by Li$_2$O evaporation during crystal growth. By using x-ray diffraction, the grown crystal was identified as $\gamma$-LiAlO$_2$ and the lattice parameters are $a = 5.1698$ Å and $c = 6.2779$ Å. The x-ray rocking curve showed the fuel width half maximum (FWHM) was 0.0452° at $2\theta = 200$. From a preliminary x-ray scan, the reflections on the LiAlO$_2$ specimen appear like a single crystal.

Transmission electron microscope (TEM) specimens oriented in different directions were prepared to identify the microstructures and defects. We need to be very careful when working with the LiAlO$_2$ TEM sample since if the electron beam is kept stationary on the material for more than a few seconds, the material will be vaporized.

![FIG. 2. TEM analysis of (001) LiAlO$_2$ sample: (a) the bright field image and its square diffraction pattern and (b) the unique cross-hatched patterns reveal a superlattice structure.](image)

![FIG. 3. Experimental setup to measure the acoustic properties of LiAlO$_2$ crystal.](image)

![FIG. 4. The propagation directions, and particle motions of the acoustic waves in the LiAlO$_2$ crystal.](image)

![FIG. 5. Time domain response of the acoustic signals of LiAlO$_2$ crystal.](image)

TABLE I. Acoustic velocities of LiAlO$_2$ crystal at the different directions.

<table>
<thead>
<tr>
<th>Direction of propagation</th>
<th>Types of waves</th>
<th>$\text{m/s}$</th>
<th>Resolution ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X$ axis</td>
<td>Longitudinal ($V_{11}$)</td>
<td>8155</td>
<td>±0.2</td>
</tr>
<tr>
<td></td>
<td>Shear ($V_{12}$)</td>
<td>3693</td>
<td>±0.1</td>
</tr>
<tr>
<td>$Z$ axis</td>
<td>Longitudinal ($V_{33}$)</td>
<td>8225</td>
<td>±0.2</td>
</tr>
<tr>
<td></td>
<td>Shear ($V_{32}$)</td>
<td>4967</td>
<td>±0.1</td>
</tr>
<tr>
<td>$+45^\circ$ rotated $Y$ cut</td>
<td>Longitudinal ($V_{44}$)</td>
<td>8221</td>
<td>±0.2</td>
</tr>
<tr>
<td>$-45^\circ$ rotated $Y$ cut</td>
<td>Longitudinal ($V_{66}$)</td>
<td>7204</td>
<td>±0.2</td>
</tr>
</tbody>
</table>

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specimen has a certain thickness, a double diffraction pattern was found. Figure 2(b) is the other (001) TEM image which showed a unique cross-hatched pattern. This grid pattern reveals a superlattice structure. The possible reason is because Li and Al atoms have very different atomic diameters and bonding length they might exchange their lattice sites in this organized way to relieve the stress. These site exchanges will cause the phase shift which results in the interference pattern. These hatched patterns are only seen when preparing the specimen looking in the (001) direction. When viewed in the other directions, these patterns are not visible.

In order to investigate the acoustic properties, including the acoustic velocities and stiffness constants of LiAlO₂ crystal, appropriate crystallographic orientations must be determined. Several principal X, Z-cut, and ±45° rotated Y-cut (rotating a Y-cut specimen around the X axis) specimen are prepared from the as-grown (100) LiAlO₂ crystal. The rotated Y-cut specimens were selected from the crystalline planes specified in the IEEE standard. Since the acoustic velocity is a function of the propagation direction, the propagation direction must be very accurate for determination of the acoustical physical constants.

Precisely cut and measured 10.0 mm LiAlO₂ cubes were manufactured to evaluate their acoustical properties. The time-based pulse-echo transmission technique was employed to measure the acoustic velocities of LiAlO₂ material. Two ultrasonic transducers were used to generate the acoustic waves, one (Panametrics V1091, 5 MHz, 1/4 in.) is for the longitudinal mode and the other one (Ultran SWC18-5, 5 MHz, 1/4 in.) is for the shear mode. The ultrasonic source and receiver are mounted on the opposite sides of the specimen. Honey serves as a couplant between the longitudinal transducer and the specimen and Panametrics SWC is the couplant for the shear wave transducer. The couplant is very thin so it does not affect the velocity measurements. If the mounting is bad, some air might remain in the couplant. This affects how much acoustic energy is transferred into the sample and makes the acoustic signal weaker. The experimental setup is shown in Fig. 3. The orientation of the shear mode transducer would allow maximizing or minimizing of various shear modes depending on the mounting angle with respect to the axis of the specimen.

Acoustic velocities measured in a temperature control environment, 26±0.5 °C are summarized in Table I. Figure 4 showed the propagation directions and particle motions of the acoustic waves in the LiAlO₂ crystal. Figure 5 is the time domain responses of the acoustic signals propagating along the different directions. The measurement errors are given by the measurement accuracy of the specimen thickness, and temperature fluctuation. Based on the Bar-Cohen’s estimate, the maximum error of velocity estimation induced by the temperature fluctuation is about 0.15%. It was found that the acoustic velocities of LiAlO₂ are much higher than the current piezoelectric crystals, including quartz, LiNbO₃, and Langasite family materials.

As LiAlO₂ belongs to the tetragonal structure, it can be characterized by 6·X₂ symmetric matrix with six stiffness constants, $C_{ij}$ ($i, j = 1, 2, 3$). By using Brown and Cheadle methods, the elastic constants can be extracted from the longitudinal and shear waves velocities at the symmetry axes, and the longitudinal wave velocities at ±45° to the symmetry axes. Table II is the stiffness constant $C_{ij}$ ($i, j = 1, 2, 3$) of LiAlO₂ crystal at room temperature.

In summary, Czochralski growth of LiAlO₂ single crystals was investigated. An organized cross-hatched pattern which reveals the superlattice structure was found in the c-axis TEM specimen. This pattern might be related to Li and Al atoms exchanging their lattice sites and causing the phase shift in the TEM image. The exact formation mechanism is still under investigation. The acoustic velocities and stiffness constant of LiAlO₂ crystal were determined. We consider carefully the proper propagation directions and modes to accurately determine the material constants. Several principal X-, Z-cut, and ±45° rotated Y-cut specimens for determining the constants are prepared from the as-grown (100) LiAlO₂ crystal. Our work forms the basis for studying the applications of the LiAlO₂ material to ultrasonic devices, such as SAW devices, resonator, bulk wave filter, sensors, and transducers. Further work is required to optimize the growth process, and to maximize accuracy in measuring the arrival time of the signal.

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| Table II. Stiffness constant $C_{ij}$ ($\times 10^8$ N/m²) of LiAlO₂ crystal at 26 °C. |
|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|
| $C_{11}$                      | $C_{13}$                      | $C_{44}$                      | $C_{66}$                      | $C_{12}$                      | $C_{11}$                      |
| 173.24±0.70                  | 176.23±0.70                  | 64.27±0.26                   | 35.53±0.07                   | 26.08±0.1                    | 48.83±0.20                   |