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Improvement in the quality of $LiCaAlF_6$ single crystal as window material

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Abstract

Three-in. size $LiCaAlF_6$ (LiCAF) single crystals were successfully grown by the Czochralski method. Both measurements of the transmission spectra in the VUV regions and the X-ray rocking curve analysis showed that the crystallinity of LiCAF single crystal was improved by the annealing. Optical absorption measurements in the UV/VIS spectral regions following X-ray irradiation were performed in order to compare the radiation damage with a lithography-grade CaF_2 crystal.

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1. Introduction

Much of the tremendous progress in integrated circuit technology and performance over the past 30 years has been fuelled by the progress in lithography [1]. The ability to print increasingly smaller features has enabled higher speed transistors, higher packing densities and lower power dissipation in CMOS circuits [2]. In pursuit of ever smaller feature sizes in lithographic techniques it was necessary for the semiconductor industry to move from the excitation mercury UV lamps operating at the g-line wavelength, and later at the i-line, to the shorter wavelength pulsed 248 nm light available from the KrF excimer lasers. Steppers utilizing 193 nm light from the ArF excimer lasers are now being introduced and SEMATECH, a forum comprised of the major silicon device manufacturers world-wide, have designated 157 nm as the route to realize device structures of 100 nm and below [3]. A very bright source for this wavelength is the molecular fluorine laser, often misleadingly referred to as an excimer laser

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because with a suitable change of optics and gas mix it operates in the same device as rare gas halide lasers [4,5]. One of the most serious problems in realizing a 157 nm based system is the development of suitable optical materials for lenses and other optical components. Although 248 and 193 nm based systems could be realized using fused silica and CaF_2, a new material is required for 157 nm based systems because of the limitation of fused silica transparency. In fact, a 2-mm-thick UV-grade fused silica plate transmits less than 10% at 157 nm [6]. In particular, for an all-refractive design 157 nm laser source, a second material other than CaF_2 is strongly required. Primary candidates for a second material were LiF and MgF_2; however, they have several disadvantages such as fragility, a hygroscopic nature and large birefringence [7].

Not only the above binary fluorides, but also the complex fluoride single crystals, such as Colquiriite- and Perovskite-type fluorides, also present many advantages as optical materials, because of their unique properties, such as a large band gap. However, detailed characteristics of complex fluoride single crystals have not yet been well investigated, mainly because the growth of these crystals is difficult. For the growth of these crystals, a fluorination process using gases such as HF [8] is usually performed in order to purify both raw materials and growing crystals. We previously reported the growth of Ce:$LiCaAlF_6$ (LiCAF) crystals without either the use of HF gases or the hydrofluorination of raw materials [9].

In the present work, we describe the growth process of large-size $LiCaAlF_6$ single crystal as window material by the Czochralski (Cz) method under modified growth conditions and we point out how to improve the quality of LiCAF single crystals.

2. Growth of LiCAF crystal

Crystal growth was performed in a vacuum-tight Cz system equipped with an automatic diameter control system. The resistive heater and thermal insulators were made of high-purity graphite. The starting material was prepared from commercially available fluoride powders (>99.99%). The starting material was placed into a Pt crucible. Vacuum treatment was performed prior to the growth. The system was heated from RT to 700 °C for 12 h under vacuum ($\approx 10^{-3}$ Pa). Both rotary and diffusion pumps were used so as to achieve a pressure of $\approx 10^{-3}$ Pa and to effectively eliminate moisture and oxygen traces from the growth chamber and starting materials. Subsequently, high purity CF_4 gas (99.99%) was slowly introduced into the furnace. Thereafter, the starting material was melted at approximately 820 °C. The pulling rate was 0.8–1.0 mm/h and the rotation rate was 8–15 rpm. Growth orientations were controlled using *a*-axis oriented undoped LiCAF seed crystals. After the growth, the crystals were cooled down to RT at a rate of 30 °C/h.

In the case of 3-in. size LiCAF crystal growth, although the diameter of the grown crystal was controlled precisely, the formation of inclusions could not be avoided. One of the possible reasons for the formation of inclusions is the instability of the growth interface between the melt and crystal. One way to improve this instability is to increase the crystal rotation rate. Another possible reason is the descent of the melt level. When the melt level changes drastically, the temperature condition around the growth interface also changes drastically. One way to keep it constant is to raise the crucible with the growth of the crystal. In this condition, the inclusions could be avoided, but many cracks appeared in the grown crystal. This is

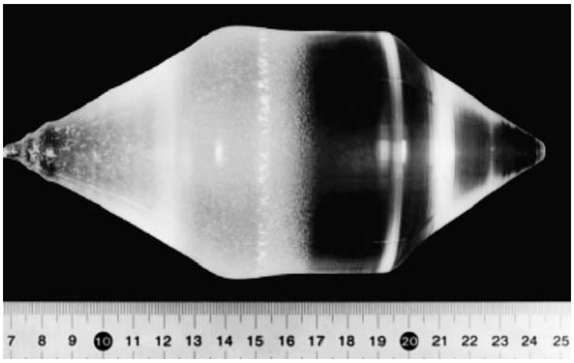

Fig. 1. As-grown $LiCaAlF_6$ single crystal 3-in. in diameter without inclusions.

probably due to the occurrence of thermal stress in a grown crystal, since it was located at a position where the temperature gradient was high during the cooling process. In order to avoid cracks the grown crystal and the crucible were lowered to their positions after the crystal growth process and the grown crystal was cooled at the position where temperature gradient was lower. Fig. 1 shows a LiCAF single crystal with 3-in. diameter, free from cracks and inclusions. The surface of the shoulder part was adhered slightly by the vaporized white material composed of LiF and AlF_3 during crystal growth, while the crystal itself was transparent.

3. Annealing effect

LiCAF crystal grown by the Cz method was cut parallel to the *c*-plane with the thickness of 10.0 mm. The *c*-plane was determined by an X-ray diffraction using Laue transmittance photograph. This wafer was arranged to the sample with the dimension of $\varnothing$30.0 mm × 10.0 mm for annealing process. Both surfaces ($\varnothing$30.0 mm) were polished as the mirror surface by a mechanochemical method. Using this sample, several measurements such as transmission in the VUV region and X-ray rocking curve (XRC) were performed before and after annealing.

Annealing was carried out in a furnace with rotary and diffusion pumps. Similar to the Cz growth process, after vacuuming at the pressure of $\sim 10^{-3}$ Pa, high-purity Ar gas (99.9999%) was introduced. Subsequently, the temperature was increased to 700–750 °C during 2 days and was hold for 8 days. Then the crystal was cooled down to RT for 2 days. As the annealed sample was covered with a white substance (Fig. 2), the sample was polished once more to get the mirror surface for the measurements. Fig. 3 shows the transmission spectra in the VUV region for LiCAF crystal before and after annealing. As can be seen, the transmission of the LiCAF crystal was improved by the annealing (transmission was increased from 82.1% to 84.8% at 157 nm). This might be due to the decrease of the scattering centre inside the as-grown LiCAF crystal. The crystal quality of the grown crystal was characterized by XRC

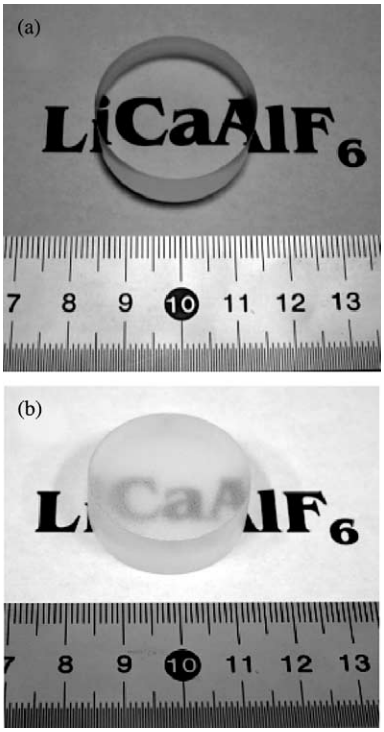

Fig. 2. $LiCaAlF_6$ samples (a) before and (b) after annealing.

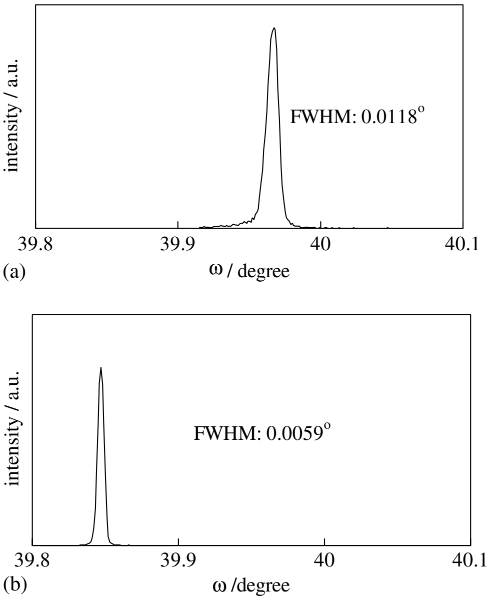

Fig. 3. Transmission spectra in the VUV wavelength region for $LiCaAlF_6$ single crystal before and after annealing.

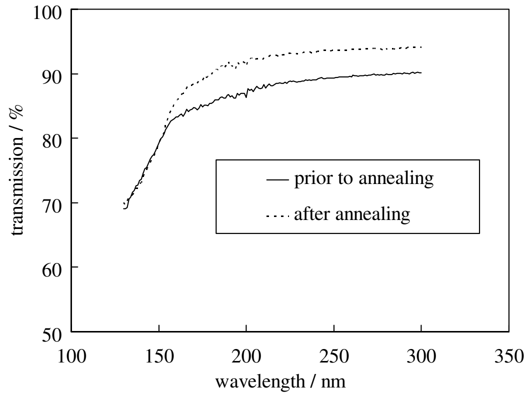

Fig. 4. X-ray rocking curve (ω scan) of $LiCaAlF_6$ (0 0 8) single crystal; (—) before and (- - -) after annealing process.

measurement. ω scan has carried out for the reflection from (0 0 8) plane corresponding to the $\langle 001 \rangle$ direction. The spectra for LiCAF crystal before and after annealing are shown in Fig. 4. It is shown that the FWHMs in LiCAF before and after annealing were measured to be 0.0118° and 0.0059°, respectively. According to the result of the measurement, the crystallinity of LiCAF sample was improved by the annealing.

4. Doping of Mg^{2+} in LiCAF

Window materials in the optical lithography systems must resist an intense UV/VUV laser irradiation without changing their transmission properties. In order to check this energy resistance, X-ray induced radiation damage test was performed. For comparison, $KMgF_3$, $BaLiF_3$ and high-quality (lithography grade) CaF_2 single crystals were also measured. In the case of LiCAF, Mg^{2+} doping decreased the amplitude of the F-centre absorption band (damage) and the optimum doping concentration was found to be about 0.2 mol% of MgF_2 in the melt [10]. The transmission spectra of the samples were measured by a Jasco V-530 UV/VIS spectrophotometer in the 190–1000 nm spectral region—before (T_0) and immediately after (T_{irr}) an irradiation procedure and the induced absorption

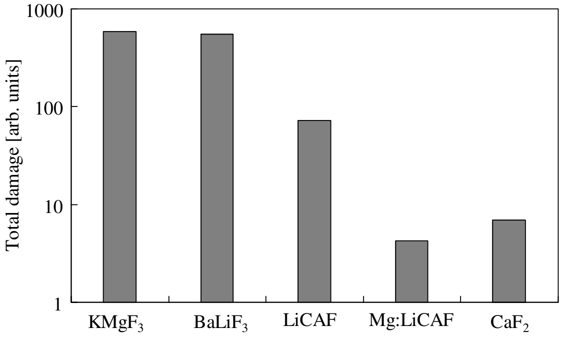

Fig. 5. The total damage (the integral of the induced absorption) for $KMgF_3$, $BaLiF_3$, $LiCaAlF_6$, $Mg{:}LiCaAlF_6$ and CaF_2 single crystals by the X-ray irradiation.

$$\mu(\lambda) = \ln(T_0(\lambda)/T_{irr}(\lambda)) \tag{1}$$

was calculated. It should be taken into account that the samples have high absorption coefficient against X-ray. It is typically achieved in LiCAF below 1 mm thickness using standard attenuation calculation according to Ref. [11]. In order to compare, all the samples were prepared with the same thickness of about 2 mm. Irradiation was accomplished by an X-ray tube (25 kV, Rigaku diffractometer). In the case of the induced absorption measurements subsequent irradiation doses were set at 240 Gy. The total damage (M) was defined as follows which value means the integral of the induced absorption

$$M = \int_{\lambda_1}^{\lambda_2} \mu(\lambda)\,d\lambda \tag{2}$$

The total damage was calculated from $\lambda_1 = 200$ nm to $\lambda_2 = 1000$ nm. Fig. 5 shows the total damage for the above fluoride crystals. While large damages appeared in the $KMgF_3$ and $BaLiF_3$ crystals after X-ray irradiation, Mg-doped LiCAF had almost same resistance as high-quality CaF_2 crystal.

5. Conclusion

Three-in. size LiCAF single crystals pure and doped with MgF_2 were successfully grown by the Cz method under a CF_4 atmosphere. Both measurements of the transmission spectra in the VUV regions and the XRC analysis were performed before and after the annealing. Transmission was increased from 82.1% to 84.8% at 157 nm and the FWHM was improved from 0.0118° to 0.0059° by the annealing. Thus, the crystallinity of LiCAF single crystal was improved by the annealing. Mg doping decreases the amplitude of the F-centre absorption band. It is proposed that Mg^{2+} partly occupies Li sites. Thus, it introduces an excessive positive charge in the cation sublattice, which can reduce the concentration of fluorine vacancies in the process of crystal growth and consequently the concentration of F centres after an X-ray irradiation. As a result, Mg-doped LiCAF had almost same resistance as high-quality CaF_2 crystal.

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