3Pb1-5

Growth of spherical lithium tetraborate crystal using lotus effect
ロータス効果を用いた四ほう酸リチウム球状結晶の育成

Ryuichi Komatsu†, Akira Nadatomo, Kohei Ikemura, Hideyuki Okamura,Harutoshi Asakawa, (Grad. School of Sci. & Tech. for Innovation, Yamaguchi Univ.)
小松隆一†，灘友晃，池村康平，岡村秀幸，麻川明俊，（山口大院創成科学研究科）

1. Introduction

Silicon, compound semiconductors and oxide crystals are mainly grown by the Czochralski (CZ) method and processed into wafers. Since the cutting loss in the wafer fabrication process is more than half of the total crystal growth[1)], the development of a cut-free crystal growth method and a shaped crystal growth method for devices has been actively pursued[2-4)].

Recently, Nakayama *et al*[5)]. have developed a new type of high sensitive gas sensor using ball SAW sensor by the ultramultiple roundtrip propagation of a SAW on quartz crystal.

However, fabrication of spherical piezoelectric crystals is complicated and will be a problem for development to solve since they are fabricated from bulk crystals. Therefore, direct growth of spherical piezoelectric crystals is important for application.

A drop tower method [2)] is one of the methods to grow directly spherical Si crystals, but spherical oxide crystals cannot be grown by this method because most of the oxide crystals are vitrified due to high undercooling during the fall. There is another method of growing spherical crystals under microgravity, but it is not suitable for mass production. The only possible method is to use a substrate repelling the melt to obtain spherical oxide crystals [6)].

We have chosen a physical approach of controlling the wettability of the melt by fabricating a relief structure into the substrate to grow spherical oxide crystals. Cassie-Baxter theory [7)] states that the contact angle of a liquid varies depending on the relief structure on the substrate surface (lotus effect). However, there have been no reports of controlling the wettability of oxide melt by the relief structure of the substrate.

In this paper, we describe the preparation of porous structures and in-situ observation of lithium tetraborate ($Li_2B_4O_7$)[8)] melts at high temperature, especially the change of contact angle between the melt and the substrate. Next, the growth of lithium tetraborate spherical crystals with a larger electromechanical coupling coefficient than that of quartz on these substrates is reported.

2. Experimental

2.1. Fabrication of porous carbon substrates and evaluation of $Li_2B_4O_7$ melts wettability

The porous substrates were prepared by mixing liquid resol-type phenolic resin and poly(methyl methacrylate) (PMMA) spherical microparticles, which were cured by heating. Specifically, liquid resol-type phenolic resin and PMMA spherical microparticles (5 μm in diameter) were mixed at a ratio of 2:1 by weight, shaped into a plate and heated at 130-160°C for at least 30 minutes to cure the resin. Next, the surface was polished with polishing powder of #2000 to make it smooth. Then, it was carbonized after heating at 1000°C for 2 hours (heating rate 250°C/h, cooling rate natural cooling) in a nitrogen atmosphere. The wettability of lithium tetraborate melt on the prepared substrate was evaluated from the contact angle and its change over time using a high temperature in-situ observation microscope [9)].

2.2 Growth of spherical $Li_2B_4O_7$ crystal

Raw material with 13 – 15 mg was placed on the porous carbon substrate for melting and coagulation. Firstly, the temperature was raised to 950°C (300°C/h), and then the temperature was kept at 950°C for 30 minutes to melt the raw material sufficiently. Since the degree of undercooling of lithium tetraborate was high, the cooling rate was changed for solidification. The grown spherical crystals were polished and observed under a polarized light microscope to examine the internal structure. The obtained crystals were identified by XRD.

3. Results and discussion

3.1 Fabrication of porous carbon substrates and in-situ observation of melting liquid on them

The SEM photograph of the prepared substrate is shown in Fig. 1. As shown in Fig. 1, the porous structure was successfully fabricated. Only carbon was detected in EDAX analysis.

The XRD result shows that the substrate is composed of amorphous carbon. Therefore, the porous amorphous carbon substrates are successfully fabricated. The photographs of the lithium tetraborate melt during the observation are shown in Fig. 2. The liquid is spherical on the porous substrate. The contact angle was about 140° by the θ/2 method and no change in the contact angle was observed by in-situ observation up to 3 hours.

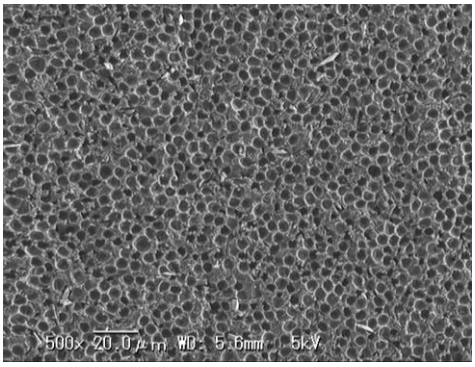

Fig. 1 SEM image of porous carbon surface

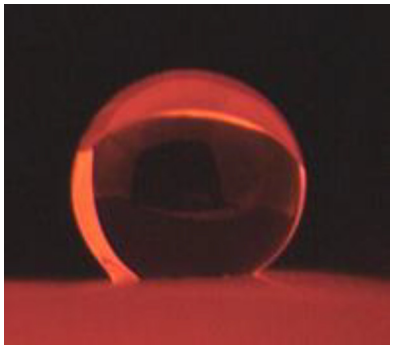

Fig. 2 Spherical $Li_2B_4O_7$ melt on porous substrate

3.2 Growth of spherical $Li_2B_4O_7$ crystal

Fig. 3 shows the grown crystals and Fig. 4 shows polarized light micrographs of the grown crystals. From XRD, it was found that the grown spherical crystals were composed of lithium tetraborate. However, grown crystal is polycrystalline as shown in Fig. 4. The intersection point indicated by the arrow A in this figure is the starting point of crystal growth, which is considered to be the point of contact between the substrate and the melt, from which nucleation occurred and crystal growth proceeded. Therefore, it is presumed that the control of nucleation during crystal growth is important for single crystal growth.

E-mail address: r-komats@yamaguchi-u.ac.jp

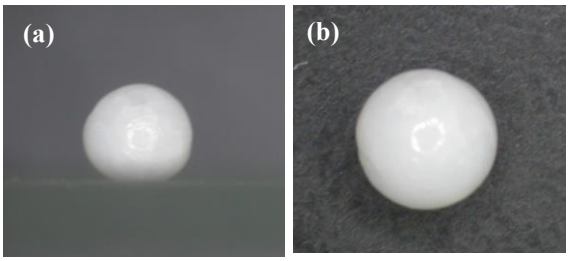

Fig. 3 Grown $Li_2B_4O_7$ crystal observed from the side (a) and top (b).

Fig. 4 Polarized micrograph of grown crystal

4. Conclusions

Spherical lithium tetraborate crystals were grown on porous carbon substrates with controlled wettability. The spherical lithium tetraborate crystals were not single crystals, but polycrystals consisting of a few grains or twins.

The suppression of polycrystallization of the crystal nuclei will be investigated in the future to obtain single sphere oxide crystal.

References

1. T. F. Cizsek, J. Crystal Growth 66 (1984) 655.
2. W.R. McKee, IEEE Trans. Components, Hybrids, Manuf. Technol. 5(1982) 336.
3. C. Okamoto *et al*., Jpn. J. Appl. Phys. 44 (2005) 7805.
4. H. Machida, K. Hoshikawa, T. Fukuda, Jpn. J. Appl. Phys. 31 (1992) L9746.
5. Nakayama *et al*., Jpn. J. Appl. Phys. 56(2017) 07JC04.
6. I. Hide *et al*., J. Crystal growth 79 (1986) 583.
7. Cassie and Baxter, Trans. Faraday Soc., 40 (1944) 546.
8. T. Katsumata *et al*., J. Crystal Growth 125 (1992) 270.
9. H. Itoh *et al*., J. Crystal Growth 401 (2014) 748.