J.Sehem.Soc. *66*(6)411–418(2001)
JSCS–2869

UDC 553.52:548.2
Original scientific paper

The growth of sapphire single crystals

ALEKSANDAR GOLUBOVIĆ[*#], SLOBODANKA NIKOLIĆ[*], STEVAN DJURIĆ[**] and ANDREJA VALČIĆ[***]

**Institute of Physics, Pregrevica 118, P.O. Box 57, YU-11001 Belgrade, **Faculty of Mining and Geology, Djušina 7, P.O. Box 162, YU-11000 Belgrade and ***Faculty of Technology and Metallurgy, Karnegijeva 4, YU-11000 Belgrade, Yugoslavia*

(Received 8 November 2000, revised 14 March 2001)

Sapphire (Al_2O_3) single crystals were grown by the Czochralski technique both in air and argon atmospheres. The conditions for growing sapphire single crystals were calculated by using a combination of Reynolds and Grashof numbers. A critical crystal diameter d_c = 20 mm and the critical rate of rotation $_c$ = 20 rpm were calculated from the hydrodynamics of the melt. The value of the rate of crystal growth was experimentally found to be 3.5 mm/h. According to our previous experiments, it was confirmed that three hours exposures to conc. H_3PO_4 at 593 K was suitable for chemical polishing. Also, three hours exposure to conc. H_3PO_4 at 523 K was found to be a suitable etching solution. The lattice parameters a = 0.47573 nm and c = 1.29893 nm were determined by X-ray powder diffraction. The obtained results are discussed and compared with published data.

Keywords: Czochralski technique, sapphire, growth, single crystal, etching.

INTRODUCTION

A sapphire single crystal is a good insulator with a band gap of about 9 eV.[1] It is chemically stable and remains transparent even after exposures to high doses of radiation and high-energy electron beams. These properties have led to its use in technological applications including such electronic devices as hot-electron tunnel transistors. As an optical material, sapphire has wide transmission range, spanning the ultraviolet, visible and infrared regions. It has, therefore, been used as an optical window material.[2] In addition, single crystal Al_2O_3 is a model compound for chemisorption studies of oxygen on aluminium and the oxidation of aluminium metal.[3] For years, its electronic structure has been the subject of numerous experimental investigations.[4–9]

The atomic structure of sapphire, $-Al_2O_3$, is typified by that of chromium sesquioxide, Cr_2O_3.[10] It has rhombohedral symmetry with two molecules in the primitive cell. The space groups is D^6_{3d}. The corresponding hexagonal unit cell is a

Serbian Chemical Society active member.

larger cell containing 12 Al and 18 O atoms with $a = 0.476$ nm and $c = 1.300$ nm.[10] The cell has the S_6 point group symmetry with respect to its centre.

Al_2O_3 is a very desirable substrate material for $YBa_2Cu_3O_7$ high T_c supper-conducting microwave devices applications, such as high Q resonators, delay lines, and infrared bolometers, because of low microwave loss, good thermal conductivity, high mechanical strength,[11,12] low cost in comparison to $SrTiO_3$, MgO and yttrium-stabilized zirconia (YSZ), and large size availability. However, the strong chemical reaction of Al_2O_3 with $YBa_2Cu_3O_7$ at high temperature is the main obstacle to many deposition techniques.[13] A sapphire substrate is also a promising material for $LiNbO_3$ optical-waveguide film.[14] The dopant-modulated bulk crystals can become a new class of materials. Recently, there appears to be significant interest in obtaining, *in situ*, crystals with variable structures *via* melt growth. The growth and application of sapphire single crystals, activated by titanium and chromium ions,[15] in laser engineering has been alloted a large amount of research time. The aim of the research presented here was, besides studying the experimental conditions required to obtain a flat interface, to obtain Al_2O_3 single crystals.

EXPERIMENTAL

Sapphire single crystals (Al_2O_3) were grown by the Czochralski technique using a MSR 2 crystal puller, as described previously.[16] The atmosphere used was air or argon. The starting materials were powdered Al_2O_3 (Koch&Light) purity 4N and ZrO_2 (Koch&Light) purity 4N for isolation. The purity of the argon (Tehnogas) was 4N. The iridium crucible (4 cm diameter, 4 cm high) was placed into an alumina vessel surrounded by ZrO_2 wool isolation. Double walls were used to protect the high radiation. To decrease the radial temperature gradient in the melt, alumina was mounted around all the system. The pull rates were generally in the range 3–12 mm/h, and the best results were obtained with a pull rate of 3.5 mm/h. The crystal rotation rates were between 20 and 50 rpm. The best results were obtained with a crystal rotation of 20 rpm. The crucible was not rotated during the growth. After the growth run, the crystal boule was cooled at a rate of about 50 K/h down to room temperature.

Various solutions of H_3PO_4 at different temperatures and exposure times were tried for chemical polishing and etching. For chemical polishing, exposure to a solution of H_3PO_4 at 593 K for 3 h was confirmed to be suitable, as was found in our previous work.[17] Exposure for three hours to an 85 % solution of H_3PO_4 at 523 K was also found to be suitable for etching.[17]

All the obtained crystal plates were observed in polarised light to reveal striations.

The chemical compositions of the products were determined by powder XRD analysis. All the samples were examined under the same conditions, using a Philips PW 1729 X-ray generator, a Philips 1710 diffractometer and the original APD software. The radiation source was an X-ray LLF tube with copper radiation and a graphite monochromator. The radiation was CuK $_1$ = 0.15405 nm. The anode tube load was 40 kV and 30 mA. Slits of 1.0 and 0.1 mm were fixed. The samples were pressed into standard aluminium frames and measured in the 2 range from 10º to 100º. Each 1/50º (0.02º) was measured for 0.5 s. For product identification, the MPDS program and JCPDS (ASTM) card files were used.

RESULTS AND DISCUSSION

Growth from the melt is one of the most important techniques for producing advanced materials. A successful growth requires the control of heat and mass transfer in the liquid and through the phase boundaries. In the case of the Czochralski technique (CZ), different types of convection are generated in the melt: natural convection due to density differences in the gravity field and to thermocapillary forces at the melt-gas interface, and forced convection caused by the rotation of the crystal and/or the crucible.[18,19]

The hydrodynamics of a melt are governed by buoyancy-driven convection or free convection, by forced convection due to crystal rotation, and by thermocapillary surface convection. Three dimensionless numbers can describe all these flows: the Grashof (*Gr*), Reynolds (*Re*) and Marangoni (*Ma*) numbers. It can be said that the depth of the melt influences the Grashof number, the rotation rate of the crystal modifies the Reynolds number, and the temperature gradient over the surface of the melt acts on the Marangoni number.[20] Several growth parameters can be modified simultaneously to obtain a change in the hydrodynamics of the melt.

The crucible is considered to be stationary during crystal rotation at a constant rate. Tangential stresses generated by surface tension gradients are applied to account for Marangoni flow, while no flow is allowed normal to the melt meniscus. Marangoni flow is given by Eq. (1)

$$Ma = -(\quad / \quad T) \quad T\,(R - r)\,(\qquad)^{-1} \qquad (1)$$

where (/(*T*) – temperature coefficient of surface tension; *T* – temperature difference ($T_{crucible} - T_{mp}$); *R* – crucible radius; *r* – crystal radius; – melt density; – kinematic viscosity, and – thermal diffusivity of the melt.

Conduction and convection caused by pulling are included in the crystal and pull rod. To simplify the current analysis, it was chosen to neglect the effects of internal radiation through the crystal. As has been pointed out by different authors,[18,19] the crystal rotation rate and the axial temperature distribution are two very important parameters, which affect the shape of the interface. Both of them are critical parameters which drastically modify the *Re* and *Gr* numbers, respectively. Therefore, these two growth parameters must be taken into account in order to understand the shape of the interface. The *Ma* number will not change significantly if a small temperature gradient exists over the surface of the melt, and so the hydrodynamics will be governed mainly by the *Re* and *Gr* numbers. This approximation was used in our papers about ($LiNbO_3$, $Bi_{12}SiO_{20}$ and $Bi_{12}GeO_{20}$),[16,21,22] and some authors have used it for Nd:YAG and Nd:GGG.[23] The Reynolds and Grashof numbers can be written by

$$Re = \quad r^2 \quad ^{-1} \qquad (2)$$

$$Gr = g \qquad T\,R^3 \quad ^{-2} \qquad (3)$$

where – rotation rate; *r* – crystal radius; – kinematic viscosity; *g* – acceleration due to gravity; – volumetric expansion coefficient of the melt; *T* – temperature difference ($T_{crucible} - T_{mp}$), and *R* – radius of the crucible. It was presumed, as Carruthers[24] did, that the kinematic viscosity at the melt/crystal interface did not change during the growth process and that the equilibrium $Gr = Re^2$ existed. There is, during this time, a flat melt/crystal interface with a critical rotation rate $_c$ and a critical diameter d_c. It was decided to use the relations derived by Carruthers for the calculations of our experimental system. These relations are in a good agreement with the experimental data of many authors[18,19] and it can be assumed that they could also be useful in our case. In this way, by applying the hydrodynamic forms, values for the critical rate of

rotation $_{c}$ = 20 rpm, and the critical diameter d_c = 20 mm were obtained. The rate of crystal growth was experimentally obtained to be 3.5 mm/h.

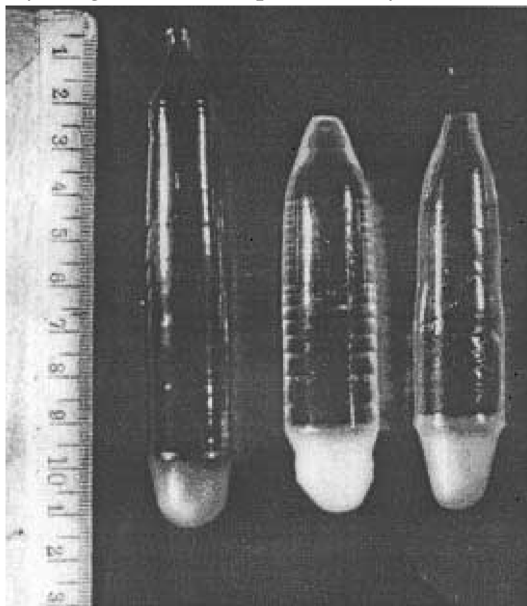

Fig. 1. A view of some of the obtained sapphire single crystals. For comparison, a ruby single crystal is shown on the left side.

Two sapphire single crystals together with a ruby single crystal (on the left side) are shown in Fig. 1. These two types of single crystals are shown together as an example of the differences in colour between crystals. The concentration of Cr^{3+} in the ruby crystal was 0.05 % wt.

An argon atmosphere during the growth run resulted in particles being inducted into the crystals. As the particles were larger than 0.1 , they scatter light,[25] and so argon is not a suitable atmosphere. The origin of this phenomena is partly due to the conversion of Al_2O_3 into aluminium suboxide.[26] After the first experiments of crystal growth in an argon atmosphere, all others were performed in air.

At temperatures higher than 1300 K, oxidation of iridium occurs. Sapphire has a high melting point (2323 K) and IrO_2 from the iridium crucible is converted to metallic Ir which falls into the melt and is incorporated into the growing crystal. The consequences are particles of 1–5 m, which scatter light and form big striations.[25] We solved this problem by flowing air, which carried the irridium away from the crystal growth zone. Some authors solved this problem by using Mo crucible,[27] as the maximum temperature for Ir crucibles is 2423 K (melting point 2725 K) compared to 2573 K for Mo crucibles (melting point 2893 K).

The sapphire single crystals were cut, chemically polished in conc. H_3PO_4 at 593 K for 3 h, and etched in conc. H_3PO_4 at 523 K for 3 h. The average number of dislocations was 5 10^2 cm^{-2}. The number of dislocation was higher in the sapphire single crystals grown with a higher rate of rotation (from 30–50 rpm) than these with lover rate of crystal growth (from 4 to 12 mm/h). In our previous studies we found average num-

bers between 15–20 10^3 cm^{-2}.[17,28] Different temperatures and exposure times in conc. H_3PO_4 were tried for chemical polishing and etching but the best results were obtained using the mentioned conditions. It was found[29] that sapphire wafers can be chemically polished and thinned in molten borax (1223–1323 K), and chemical etching in molten borax (1123–1273 K) for about 15 min. We did not work with molten borax in our experiments on polishing and etching because preference was given to a lower temperature process and satisfactory results were obtained using conc. H_3PO_4 under the above given conditions.

The polished crystal plates were observed under polarised light which showed the absence of bubbles, entrapments, non-homogeneous impurity concentrations and striations.

The structural properties were obtained using X-ray diffraction analysis of powdered samples. A Philips PW 1710 diffractometer was used in the 2 ranges from 10º to 100º. The unit cell of sapphire was calculated by the least square method using 24 reflections including more K $_2$ for 7 reflections. All the reflections correspond to Al_2O_3 crystals and gave the parameters of the rhombohedral unit cell a = 0.4759 nm and c = 1.2992 nm.[30] Some divergence from the compared results can be explained by the fact that X-ray powder diffraction analysis gives a statistical result. Our calculated results for the lattice parameters are a = 0.4757 nm and c = 1.2989 nm, which are in good agreement with published data.[2,10,29] The X-ray diffractogram for powdered sapphire is given in Fig. 2, in which the weak reflections are not marked with Mueller indices.

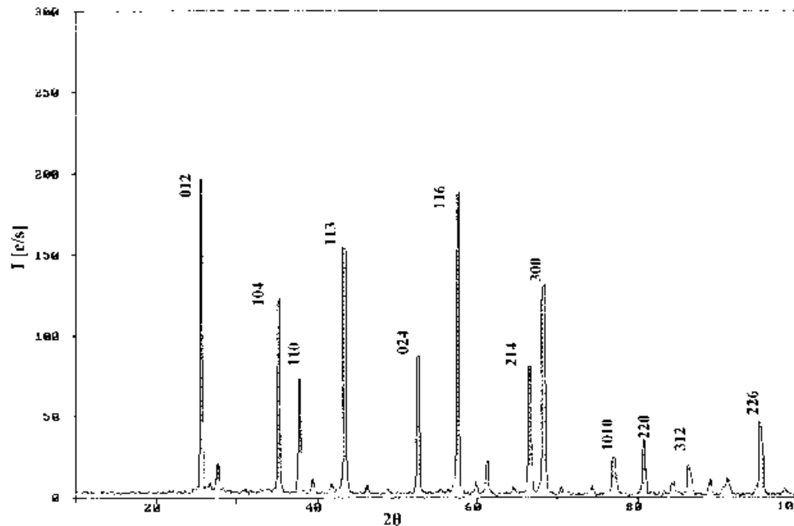

Fig. 2. X-Ray pattern of powdered sapphire single crystal.

The intensities of the reflections for some crystal planes, together with their Mueller indices and distances between the planes of the reflections are given in Table I. The intensities of the reflections from Fig. 2 are given together with published intensities for the same planes in JCPDS ("Joint Committee on Powder Diffraction Standards").

Table I. The found spacing of the lattice planes, Mueller indices and intensities for sapphire (Al_2O_3) together with comparative literature data[30]

2	$2_{lit.}$	(*hkl*)	I/I_{max}	$(I/I_{max})_{lit.}$
25.584	25.576	012	100	72
35.159	35.150	104	54.43	98
37.789	37.767	110	37.74	44
41.686	41.683	006	2.06	1
43.367	43.340	113	78.84	100
46.193	46.175	202	2.06	2
52.567	52.548	024	48.31	48
52.706			24.78	
57.515	57.498	116	96.44	96
57.669			44.64	
59.762	59.738	211	2.06	3
61.151	61.124	122	5.23	4
61.317	61.303	018	5.44	9
66.541	66.514	214	39.98	38
66.725			19.71	
68.234	68.202	300	72.59	57
68.424			32.43	
70.439	70.411	125	2.06	1
74.322	74.300	208	2.32	1
76.894	76.873	1010	8.50	17
77.257	77.234	119	5.44	10
77.482			2.46	
80.730	80.692	220	19.71	7
80.969			9.57	
84.388	84.348	223	3.22	5
84.386	86.347	312	8.24	4
89.024	88.997	0210	2.46	8
95.285	95.236	226	29.92	19
95.593			15.22	

An investigation concerning the possible use of sapphire as a substrate for superconducting material is in progress and these results, accompanied with their optical properties will be published in a future article.

CONCLUSION

The conditions for growing sapphire single crystals were calculated using a combination of Reynolds and Grashof numbers. From the hydrodynamics of the melt, a critical crystal diameter d_c = 2.0 cm and a critical rate of rotation $_c$ = 20 rpm were calculated. The value of the rate of crystal growth was experimentally found to be 3.5 mm/h.

Concentrated H_3PO_4 was shown to be suitable for both polishing and etching.

И З В О Д

РАСТ МОНОКРИСТАЛА САФИРА

АЛЕКСАНДАР ГОЛУБОВИЋ[1#], СЛОБОДАНКА НИКОЛИЋ[1], СТЕВАН ЂУРИЋ[2] и АНДРЕЈА ВАЛЧИЋ[3]

[1]Инсти̅ту̅т за физику, Пре̅гревица 118, п̅. п̅р. 57, 11001 Бео̅град, [2]Рударско-̅геолошки факул̅те̅т, Ђушина 7, п̅. п̅р. 162, 11000 Бео̅град и [3]Технолошко-ме̅талуршки факул̅те̅т, Карне̅гијева 4, 11000 Бео̅град

Монокристали сафира (Al_2O_3) су расли помоћу технике по Чохралском на ваздуху и у аргону. Услови раста монокристала сафира су израчунати коришћењем комбинације Рејнолдсовог и Грасхофовог броја. Вредности критичног пречника d_c = 20 mm и критичне брзине ротације $_c$ = 20 o/min су одређене помоћу једначина динамике флуида. Брзина извлачења кристала од 3,5 mm/h је одређена експериментално. Сагласно нашим ранијим експериментима, као средство за хемијско полирање је потврђена конц. H_3PO_4 на 593 K при излагању од 3 сата. Конц. H_3PO_4 на 523 K при излагању од 3 сата се показала као погодно средство за нагризање. Одређени су параметри решетке a = 0,4757 nm и c = 1,2989 nm помоћу рендгенске дифракционе анализе праха. Добијени резултати су дискутовани и упоређени са литературним подацима.

(Примљено 8. новембра 2000, ревидирано 14. марта 2001)

REFERENCES

1. E. T. Arakawa, M. W. Williams, *J. Phys. Chem. Solids* **29** (1968) 735
2. Z. Qiang, D. Peizhen, G. Fuxi, *J. Appl. Phys.* **67** (1990) 6159
3. D. Norman, S. Brenann, R. Jaeger, J. Stoehr, *Surf. Sci.* **105** (1981) L297
4. T. Tomiki, T. Futemma, H. Kato, T. Miyahara, Y. Aiura, H. Fukutani, T. Shikenbrau, *J. Phys. Soc. Jpn.* **58** (1988) 1486
5. A. Balzarotti, F. Antonangeli, R. Girlanda, G. Martino, *Solid State Commun.* **44** (1982) 275
6. S. P. Kowalczyk, F. R. McFeely, L. Ley, V. T. Gritsyna, D. A. Shirley, *Solid State Commun.* **23** (1977) 161
7. A. Balzarotti, A. Bianconi, *Phys. Status Solidi B* **76** (1976) 689
8. K. Codling, R. P. Madden, *Phys. Rev.* **167** (1968) 592
9. J. M. Chen, J. K. Simons, K. H. Tan, R. A. Rosenborg, *Phys. Rev. B* **48** (1993) 10047
10. J. Guo, D. E. Ellis, D. J. Lam, *Phys. Rev. B* **45** (1992) 3204
11. C. S. Chern, J. Zhao, Y. Q. Li, P. Norris, B. Kear, B. Gollois, *Appl. Phys. Lett.* **57** (1990) 721
12. B. Ullrich, I. Kulac, H. Pint, G. Leising, H. Kahlert, *Jpn. J. Appl. Phys. Part 2* **31** (1992) L856
13. M. Naito, R. H. Hammond, B. Oh, M. R. Hahn, J. W. P. Hsu, P. Rosenthal, A. F. Marchall, M. R. Beasley, T. H. Geballe, A. Kapitulnik, *J. Mater. Res.* **2** (1987) 713
14. M. Haruna, H. Ishizuki, J. Tsutsumi, Y. Shimaoka, H. Nishihara, *Jpn. J. Appl. Phys. Part 1* **34** (1995) 6084
15. V. N. Kurlov, S. V. Belenko, *J. Crystal Growth* **191** (1998) 779

16. A. Golubović, R. Gajić, S. Nikolić, S. Djurić, A. Valčić, *J. Serb. Chem. Soc.* **65** (2000) 391
17. A. Valčić, R. Roknić, S. Nikolić, *Proc. XXII Symp. ETAN in Marines*, Zadar, Croatia, 1980, p. 354
18. R. A. Brown, *Advances in Crystal Growth*, P. M. Dryburgh, Ed., Prentice-Hall, Englewood Cliffs, New York, 1987, p. 41
19. R. Ristorcelli, J. L. Lumley, *J. Crystal Growth* **116** (1992) 647
20. M. T. Santos, J. C. Rojo, L. Arizmedni, E. Dieguez, *J. Crystal Growth* **142** (1994) 103
21. A. Golubović, S. Nikolić, R. Gajić, S. Djurić, A. Valčić, *J. Serb. Chem. Soc.* **64** (1999) 553
22. A. Golubović, R. Gajić, C. Chen, A. Valčić, *J. Serb. Chem. Soc.* **65** (2000) 611
23. J. J. Derby, Q. Xiao, *J. Crystal Growth* **113** (1991) 575
24. J. R. Carruthers, *J. Crystal Growth* **36** (1976) 212
25. G. M. Loiacano, *Tunable Solid State Lasers II*, P. Hamerling, A. B. Budgor, A. Pinto, Eds., Springer-Verlag, Berlin, 1985, pp. 98–104
26. A. A. Kaminskii, B. B. Osiko, *Neorganicheski materiali*, vol. 6, Nauka, 1970, pp. 642–650
27. V. A. Borodin, V. V. Sidiriv, S. N. Rossolenko, T. A. Steriopolo, V. A. Tatarchenko, T. N. Yalovets, *J. Crystal Growth* **104** (1990) 69
28. A. Valčić, R. Roknić, S. Nikolić, *Proc. 23. Chem. Symp. of SR Serbia,* Belgrade, Yugoslavia, 1981, p. 627
29. Y. Qiang, D. Peizhen, G. Fuxi, *J. Crystal Growth* **108** (1991) 377
30. JCPDS 43-1484.