Journal of Korean Association of Crystal Growth
Vol. 9, No. 1 (1999) 29-33

Fabrication of Cr^{3+} doped sapphire single crystal by high temperature and pressure acceleration method

E.S. Choi, C.H. Jung, M.K. Kim, H.T. Kim, J.Y. Hong* and Y.T. Kim*

Institute of Ceramic Technology, NITQ, Seoul 153-023, Korea
**Department of Materials Engineering, Kyonggi University, Suwon 442-760, Korea*
(Received October 28, 1998)

고온가압 확산법에 의한 Cr^{3+} 고용 사파이어 단결정의 제조

최의석, 정충호, 김무경, 김형태, 홍정유*, 김유택*

요업기술원, 서울, 153-023
*경기대학교 재료공학과, 수원, 442-760
(1998년 10월 28일 접수)

Abstract Transition metallic Cr^{3+} ion was diffused in white sapphire {0001}, {10$\bar{1}$0} crystal plane which were grown by the Verneuil method, it enhanced and changed the physical, electrical and optical properties of sapphires. After mixing the metallic oxide and metal powder, it were used for diffusion powder. When it was used the mixing powder of metal and metallic oxide, the dopping was slowly progressed and it needed the longer duration time and higher temperature, relatively. Metallic powder was vapoured under 1×10^{-4} torr of vacuum pressure at 2050°C, first step, it were kept by the diffusion condition of 6 atm of N_2 accelerating pressure at 2050~2150°C. Each surface density of sapphire crystal are 0.2254(c) and 0.1199 atom/Å^2(a). The color of the Cr-doped sapphires was changed to red. Dopping reaction was come out more deep in the plane of {10$\bar{1}$0} than {0001}. It was speculated that the planar density was one of the factors to determine diffusion effect.

요　약 Verneuil 법에 의해 성장된 무색 sapphire {0001}, {10$\bar{1}$0} 결정면에 전이금속 Cr을 확산시키고, 물리적, 전기적, 광학적 특성을 개선하였다. 확산분말은 금속산화물 분말과 금속분말을 혼합한 후 사용하였다. 혼합분말을 사용하였을 때 확산은 오랜시간 높은 온도를 필요로 하며 상대적으로 서서히 이루어 졌다. 금속분말은 1×10^{-4} torr, 2050°C의 조건에서 1차 기화하였고 이후 2050~2150°C, 질소가압 6 atm의 확산조건에서 유지하였다. 사파이어의 표면밀도는 0.2254(c)와 0.1199 atom/Å^2(a)이었다. 확산이 이루어진 sapphire는 붉은색으로 변하였다. 고용반응은 {10$\bar{1}$0} 결정면이 {0001} 보다 더욱 깊게 확산되었고, 면밀도가 확산효과를 결정하는 주요인자이었다.

1. Introduction

The Sapphire is a single crystal of corundum α-Al_2O_3, which is a naturally producted or artificially synthesized by improved technology [1]. The crystals are grown by Verneuil, Czochralski, EFG (Edge-defined Film-fed Growth), Bridgeman, Flux, and Hydrothermal method etc [2-6].

The synthetic sapphire have good mechanical, optical, and electrical properties, so it is used for substrate of electro-optics, ultraviolet window, laser, chemical equipment, mechanical device etc [7-10]. Especially the transition material (Cr, Fe, Co, Ti, Ni) doped sapphire have appeared good color and properties [9, 11, 12]. As to the synthetic white sapphire, many research have done and productivity reaches optimum level. But colored sapphire is not sufficiently studied because there are many problems in the solid solution of dopants and growing conditions [13, 14]. If it could be diffused the transition material in the surface of synthetic white sapphire, it would enhance the optical and mechanical properties of sapphire [14, 15].

So, we try to develop the high temperature and pressure acceleration control technique which can diffuse transition metal in single crystal at the high temperature. That is developing the diffusion technique of transition metal in the crystal by control of high temperature with vacuum and pressure acceleration and then application of substrate for electro-optics which can use in laser generation and ultraviolet window, high temperature mechanical device and chemical equipment.

2. Experiment

2.1. Sapphire crystal and powder preparation

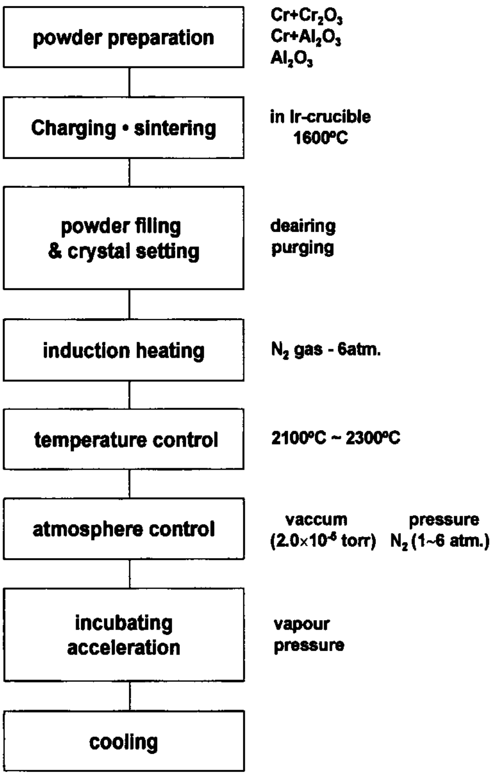

Fig. 1. Procedure of transition metal diffusion.

In Verneuil method, γ-Al_2O_3 powder is dropped with oxygen flow from the top, and hydrogen gas is burned in the middle of mixture, and the temperature of flame reaches about 2000°C moreover. If some melt is formed, it sticks to rotating seed crystal and sapphire crystal grows continuously to the preferential direction of crystal. Nevertheless some air bubble may be adulterated, this method have a merit; no contamination, continuous mass production and good workability. We chose the synthetic sapphires grown by Verneuil method, cutted the a plane of $\{10\bar{1}0\}$ and used the test piece of disk.

Metallic oxide was synthesized by precipitation method and it's composition was mainly alumina which doped with chromium oxide. Experimental procedure was Fig. 1.

Metal and oxides of Cr was used for the diffusion materials of the white sapphire. It was applied that the solution method may enhance the reactivity and effect of diffusion. Prepared power were Cr, Cr_2O_3, and Cr-Al_2O_3. The composition of Cr-Al_2O_3 was corresponded to 5 or 10 % of Cr_2O_3 for Al_2O_3, finally.

2.2. Diffusion process

The High frequency induction furnace with transistor inverter was used for heating system. In the center of induction coil, iridium crucible was setted and it was protected with the high temperature insulating material like as Alumina tube, Zirconia tube and Zirconia felt (Fig. 2). There was small viewing port on the wall of insulating tube, outersides, it was setted and sealed by quartz tube with O-ring combination. The temperature was measured by optical pyrometer and the port was sited the middle hight of Ir-crucible. Ir-crucible was filled with Al_2O_3 powder by half amount, and Cr-Al_2O_3 (Cr_2O_3 doped) powder was spreaded on that. Sapphire sub-

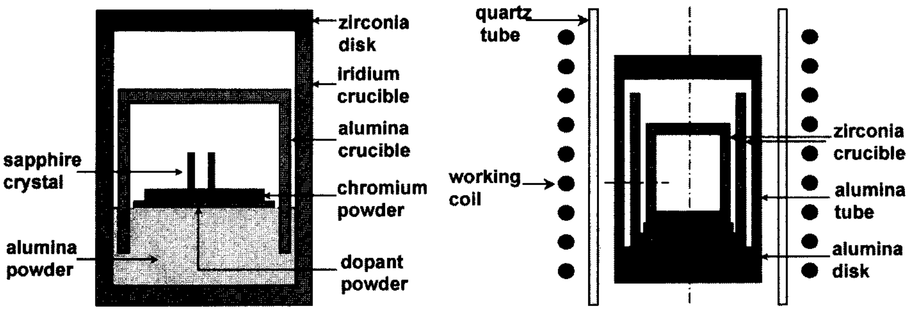

Fig. 2. Crucible apparatus of heating and pressure acceleration.

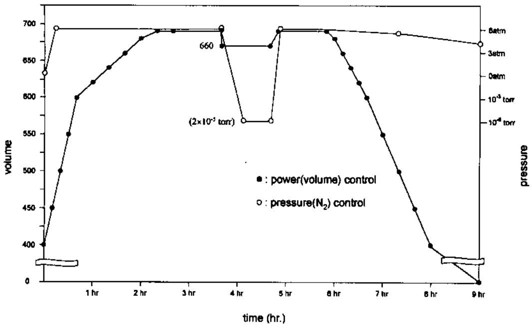

Fig. 3. Temperature and pressure control with time.

strate was put on the layer and it was covered or spreaded by proper amount of Cr_2O_3-Cr (Cr_2O_3 mixed Cr) powder. In another case we used Cr metal powder for diffusion materials. All samples were tightly closed with small space by Al_2O_3 crucible (Fig. 2).

In this system, vacuum could reach to 10^{-5} torr by rotary and diffusion pump, pressure could accelerate to 6~10 atm of N_2 atmosphere. High frequency generator elevated the temperature to 2000~2150℃ and the rate was 20℃/min by adjusting volume manually.

The schedule of controlling is in Fig. 3.

3. Result and discussion

3.1. Analysis of sapphire crystal

The chemical composition analysis of sapphire is in Table 1. There are mainly Al_2O_3 and a very small amount of CaO, MgO, TiO_2, Cr_2O_3, Fe_2O_3.

In the X-ray diffraction analysis, {0001} planer peak was gained for the vertical face to the growing direction, and $\{10\bar{1}0\}$ peak showed for parallel face. The planar density were 0.1199 atom/Å^2 (a or b plane) and 0.2254 atom/Å^2 (c plane). The thermal expansion coefficient were 7.10×10^{-6} (vertical direction) and 6.99×10^{-6} (parallel). It was related to planer density. So, it was thought that the effect of diffusion would be concerned with these.

Table 1
Chemical analysis of each sapphire

Comp.	Al_2O_3 (%)	CaO (ppm)	SiO_2 (ppm)	MgO (ppm)	TiO_2 (ppm)	Fe_2O_3 (%)	Cr_2O_3 (%)
WS	99.99	3.70	8.57	2.32	10	0.01	0
BS	99.75	3.82	8.55	2.30	9	0.25	0
RS	99.52	3.70	8.53	2.30	8	0.03	0.45
RD	99.81	3.70	8.54	2.31	9	0.03	0.16

WS: White Sepphire, BS: Comerical Blue Sapphire, RS: Ruby Sapphire, RD: Diffused Red Sapphire.

3.2. Diffusion of high temperature and accelerating pressure

The compound powder of Cr metal and Al_2O_3 may got to melting state over 2000℃. It doesn't make visual reaction. Theoretical melting temperature of Al_2O_3 is 2050℃ and Cr_2O_3 is 1990℃. Because the measuring point of temperature is the exterior surface of crucible, the temperature of inner sample may be moreover than that. In the crystal, diffusion of atoms occurs by the motion of defects and diffusion take place by vacancy, interstitialcy and semiinterstitialcy mechanism. But it is not proved, in the principle, diffusion can take place by direct-exchange and ring mechanism.

Vacancy is introduced by effect of the impure substance in the low temperature but it occurs to thermal equilibrium at the high temperature. The temperature region that vacancy is introduced by the impurity is extrinsic zone, and high temperature region that free from the impurity is intrinsic zone. When a atom jumps and moves from lattice site (unit-space) to nearest vacancy (open-space), the spatial energy of atom is able to overcome energy level. Al_2O_3 and Cr_2O_3 has been complete solid

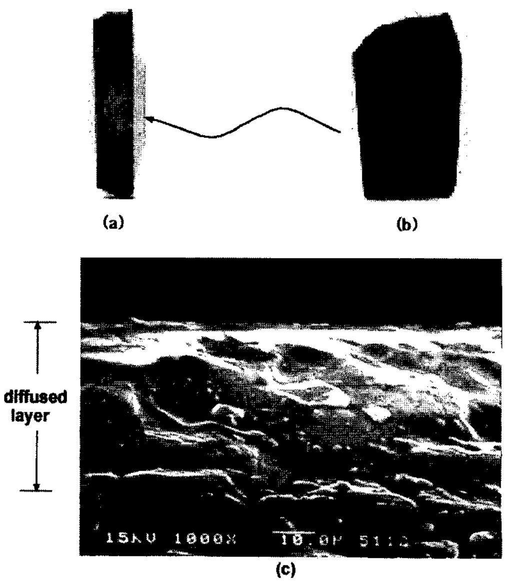

Fig. 4. Photographs of diffusion sapphire. (a) cut face (b) surface (c) SEM of cut face.

solution state between solidus line and liquidus line. In the case of Cr_2O_3 10 %-Al_2O_3 90 % composition, solid-liquid mixed zone is in the range 2055~2080℃. But the case of the Cr_2O_3 5 %-Al_2O_3 95 % composition have narrow zone at 2050~2060℃.

The diffusion effect of powder was more deep by using synthetic Cr_2O_3-Cr dopant which precipitation Cr_2O_3 powder was mixed 5~10 % content to Cr metal. It could be sure that this dopants is more stable to maintain the vapour state than using the independent Cr-metal powder.

Figure 3 shows the condition of pressure and temperature. Decrement of pressure was carried in 2150℃, which was the temperature to be directly diffused by using compound powder of Cr_2O_3 and Cr metal. As the pressure decrease, the power (volume) was come down to maintain same temperature. Vapour of Cr metal was formed at near 1×10^{-4} torr and diffusion effect was observed by re-accelerating to 6 atm. after decreased down the vacuum pressure to 2×10^{-5} torr. The better diffusion effect was obtained through careful pressure control, incubating condition and temperature control.

Figure 4 shows interface of the sapphire crystal body and the diffusion surface.

It was photograph of vertically cutted sample and showed that the diffusion degree on the surface was about 10 μm thickness.

Chemical composition of diffusion sapphire shows EPMA analysis in Fig. 5. The analysis was carried out from the surface to 30 μm inside depth and the concentration of Al_2O_3-Cr_2O_3 is in Fig. 6.

Generally, the Cr_2O_3 content of rubby sapphire was 0.45 %. In this result, it's content was to 0.16 % by diffusion of Cr_2O_3 from the surface into adequate depth. Also, in spite of using a little amounts of transition element, doping effect of color was not showed the red color sufficiently as the ruby crystal.

But Cr_2O_3 concentrations to the Al_2O_3 of diffusion

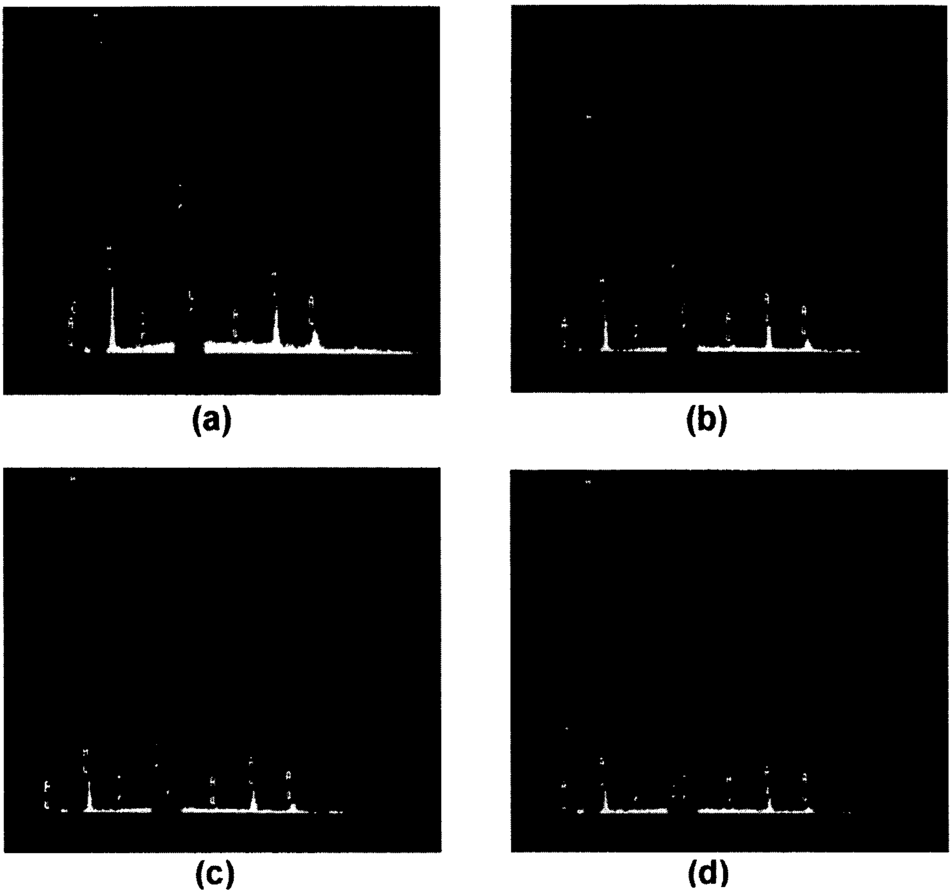

Fig. 5. EPMA analysis of diffusion sapphire with depth. (a) 5 μm (b) 10 μm (c) 20 μm (d) 30 μm from surface.

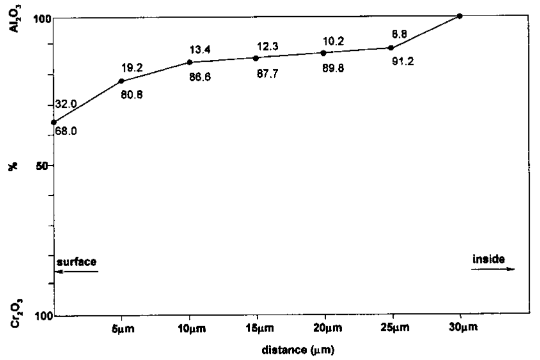

Fig. 6. Concentration composition of diffusion layer in crystal.

layer in crystal were 32 % of surface, 13.4 % of 10 μm, 10.2 % 20 μm and 0 % of 30 μm layer, respectively.

4. Conclusions

We used crystalline powder of Cr metal and Cr_2O_3 and could diffuse effectively solubility and reactivity of Cr^{3+} in sapphire single crystal under nitrogen gas pressure acceleration and high temperature.

1) The powder of Cr_2O_3-Cr dopant or Cr_2O_3-Al_2O_3 which was 10 % of Cr_2O_3 content to the Cr metal or Al_2O_3 was more stable to maintain the vapour state and more effective to diffuse in sapphire single crystal.

2) Optimum diffusion conditions of transition elements was temperature range of 2055~2060℃, vacuum of 2×10^{-5} torr and 6 atm of pressure acceleration.

3) Surface density of sapphire were 0.2254 atom/Å^2 and 0.1199 atom/Å^2 to c{0001} and a{10$\bar{1}$0} respectively, and diffusion thickness was 30 μm (a face) and Cr_2O_3 concentrations to the Al_2O_3 were from 30 % of surface to 10.2 %.

References

[1] A. Verneuil, Ann. Chim. Phys. 3 (1904) 20; Compt. Rend 135 (1902) 79.

[2] L.M. Davis, Br. Ceram. Soc. 6. (1966) 1.

[3] J.G. Grabmaier, J. Crystal Growth 5 (1969) 105.

[4] Richard A. Nyquist and Ronald O. Kagel, Infrared Spectra of Inorganic Compounds (Academic Press, New York and London, 1971).

[5] K. nassau, J. Crystal Growth 13/14 (1972) 12.

[6] R. Falkenberg, J. Crystal Growth 19 (1975) 195.

[7] C.H.L. Goodman, Crystal Growth 2 (Plenum Press, New York & London, 1978) 11.

[8] D.S. Phillips, A.H. Heuer and T.E. Mitchell, Phil. Mag. A, 42 (1980) 385.

[9] Kurt Nassau and Julia Nassau, Crystal 2, (Springer-Verlag, Berlin Heidelberg, 1980) p. 24.

[10] Kurt Nassau, The Physics and Chemistry of Color, (A Wiely-Interscience Publication, New York, Chichester, Brisban, Toronto, Singapore, 1983).

[11] Kurt Nassau, The Physics and Chemistry of Color (John Wiley & Sons Inc., New York, 1983).

[12] E. Ryshkewitch and D.W. Richerson, Oxide Ceramics (Academic Press Inc., Orlando, Florida, 1985).

[13] Peter M. Dryburgh, Brian Cockaye and Keith G. Barraclough, Advanced Crystal Growth, Prentice Hall International (UK) Ltd. (1986).

[14] Keshra Sangwal, Etching of Crystals, North-Holland Physics Publishing (1987).

[15] H. Yanagida and R. Falkeuberg, The Chemistry of Ceramics (1996) pp. 122-134.