Fabrication of Transition metal doped Sapphire Single Crystal by High Temperature and Pressure Acceleration Method

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Abstract

Transition metal Cr^{3+} and Fe^{3+} ion was diffused in white sapphire {0001}, {10$\bar{1}$0} crystal plane which were grown by the Verneuil method. It enhanced and changed the physical, electrical and optical properties of sapphires. After mixing the metallic oxide and metal powder, it were used for diffusion. Metallic oxide was synthesized by precipitation method and it's composition was mainly alumina which doped with chromium or ferric oxide. In case using metallic oxide, the dopping was slowly progressed and it needed the longer duration time and higher temperature, relatively. Metallic powder was vapoured under 1×10^{-4} torr of vacuum pressure at 1900(iron metal) and 2050(chromium)℃, first step. Diffusion condition were kept by 6atm of N_2 accelerating pressure at 2050~2150℃. Each surface density of sapphire crystal are 0.2254(c) and 0.1199atom/Å^2(a). The color of the Cr-doped sapphires was changed to red. Dopping reaction was come out more deep in the plane of {10$\bar{1}$0} than {0001}. It was speculated that the planar density was one of the factors to determine diffusion effect.

I. Introduction

The Sapphire is a single crystal of corundum α-Al_2O_3, which is a naturally producted or artificially synthesized by improved technology. The crystals are grown by Verneuil, Czochralski, EFG, Bridgman, Flux, and Hydrothermal method etc.

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 divice etc. Especially the transition material(Cr, Fe, Co, Ti, Ni) doped sapphire have appeared good color and properties. As to the synthetic white sapphire, many research have done and productivity reachs optimum level. But colored sapphire is not sufficiently studied because there are many problems in solubility of dopants and

growing conditions. So, the trial, diffusing the transition material on the surface of synthetic or natural white sapphire, is being done now.

Nowadays, jewelry crystals are exhausting but the demand grows larger every year for the progressing of cultural level. For these reason, we needs the technique by which colored sapphire would be gained easily.

In this study we try to develop the diffusion technology of transition materials to the surface of synthetic white sapphire by high temperature and pressure acceleration method.

Ⅱ. Experiment

1) Sapphire crystal and powder preparation

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 reachs about 2000℃. If some melt is formed, it sticks to rotating seed crystal and sapphire crystal grows continuously to the preference direction. Nevertheless some bubble may be adulterated, this method have a merit ; no contamination, continuous mass production and good workability. We used the synthetic sapphires grown by Verneuil method. The sapphire single crystals were cut with the $\{10\bar{1}0\}$ and {0001}plane.

Metal and oxides of Cr and Fe were used for the diffusion materials on the white sapphire. It was supposed that the solution method may enhance the reactivity and effect of diffusion. Prepared power were Cr, Fe, Cr_2O_3, Fe_2O_3, Cr-Al_2O_3, and Fe-Al_2O_3.

The composition of Cr-Al_2O_3, and Fe-Al_2O_3 were corresponded to 5 or 10% of Cr_2O_3 (or Fe_2O_3) for Al_2O_3, finally.

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 to high temperature insulating material like as Alumina tube, Zirconia tube and Zirconia felt. There was small viewing port on the wall of tube. The temperature was measured by optical pyrometer and the port was sited the middle hight of Ir-crucible. Al_2O_3 powder was filled in the Ir-crucible half amount, and sapphire substrate was put on it. The proper amount of Cr-Al_2O_3(or Fe-Fe_2O_3) powder covered the sapphire. In another case we used Cr or Fe metal powder for diffusion materials. All samples were titly closed with small space by Al_2O_3 crucible.

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. (Fig. 1, 2, 3)

Ⅲ. Result and discussion

1) Analysis of sapphire crystal

In the X-ray diffraction analysis, $\{10\bar{1}0\}$planer peak was gained for the vertical face to the growing direction, and {0001} peak showed for parallel face. The schematic drawing of sapphire structure is in Fig. 3. The planer density were 0.1199 atom/$Å^2$(a or b plane) and 0.2254 atom/$Å^2$(c plane). The thermal expansion ratio 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. Fig. 5. shows the estimating planes in the grown crystal.

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 point of Al_2O_3 is 2050℃, Cr_2O_3 is 1990℃ and Fe_2O_3 is 1550℃. Because the measuring point of temperature is the outer surface of crucible, the temperature of inner sample may be moreover than that. In the crystal, diffusion of atoms which contain defects 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 in Fig. 6. Al_2O_3 and Cr_2O_3 has been complete solid solution state between solidus line and liquidus line. In the case of Cr_2O_3 10% component, solid-liquid mixed zone have the range 2055～2080℃. But the case of the 5% component have narrow zone at 2050~2060℃.

Decrement of pressure was carried in 2150℃, which was temperature to be directly diffuse by using compound powder of Cr_2O_3 and Cr metal. Vapour of Cr metal was formed at close to 1×10^{-4}torr and diffusion effect was observed by re-accelerate after down the pressure to 2×10^{-5}torr. The better diffusion effect was obtained through careful pressure control, incubating condition and temperature control. Fig. 7. shows some diffused samples, (a) is diffused on unpolished and (b) is mirror polished face. We could sure that the former is more deep than the latter. In another observation, the diffusion degree of each surface was about 5㎛(c-plane) and 10㎛(a-plane) thickness. From these results, it could be supposed that diffusion of transition elements depends on surface density. 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 observed. But color effect was not showed sufficiently in case of using solid powder.

Ⅳ. Conclusion

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 and high temperature.

1) Optimum diffusion conditions of transition elements into sapphire single crystal was under 10wt% Cr_2O_3 content of powder which mixed with Cr metal, temperature range of 2055~2060℃, vacuum of 2×10^{-5}torr and 6 atm of N_2 gas pressure.

2) In experiment using powder of Al_2O_3 and Cr metal, vapour was formed in crucible and diffusion effect of Cr in sapphire showed red color under controlled decrement acceleration pressure condition.

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 were 5㎛(c face) and 10㎛(a face) respectively.

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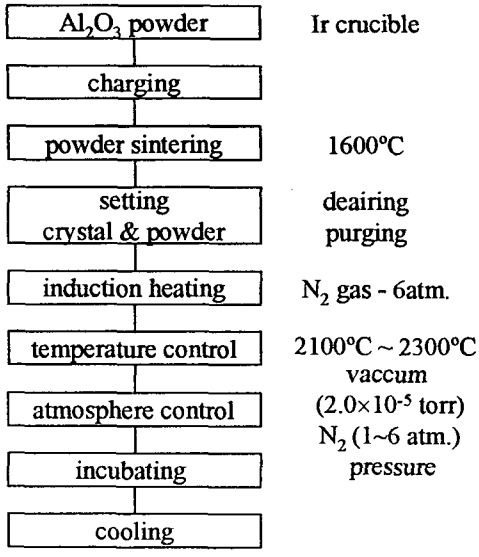

Fig. 1. Experimental procedure

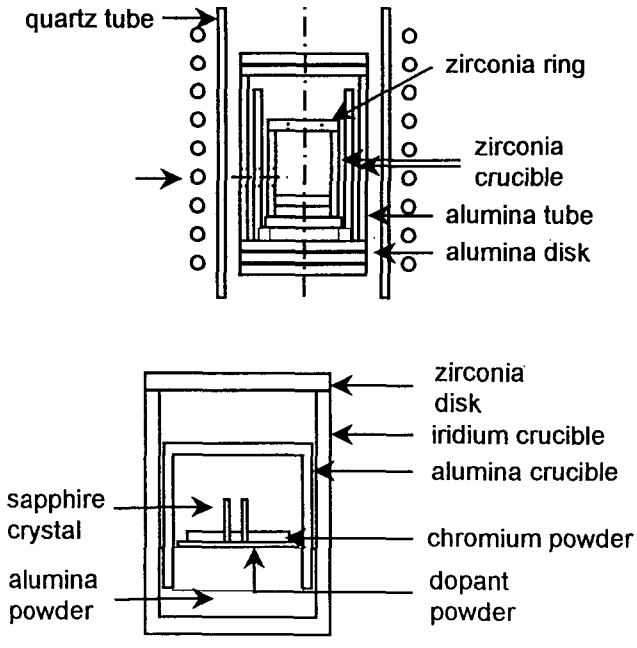

Fig. 2. Schematic diagram of induction heating equipment
(a) heating zone (b) sample setting

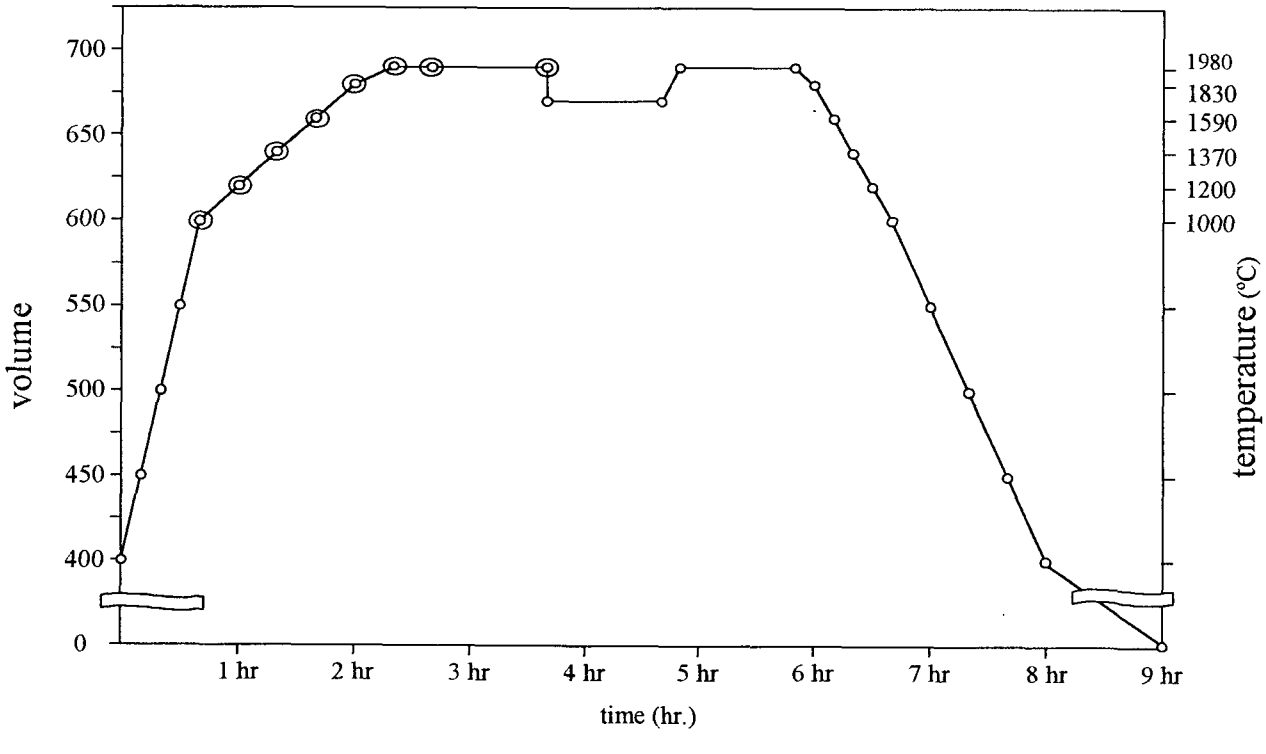

Fig. 3. Diagram of heating schedule

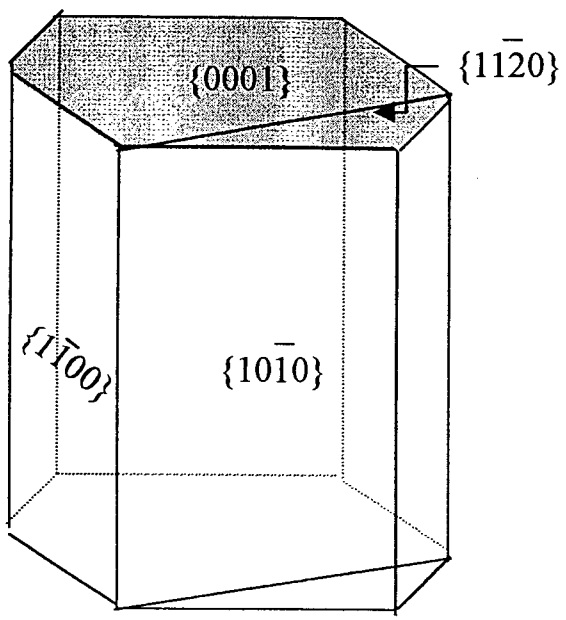

Fig. 4. Hexagonal crystal structure of synthetic sapphire

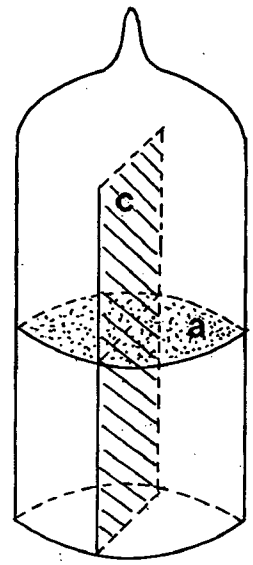

Fig. 5. Estimated planes of sapphire single crystal

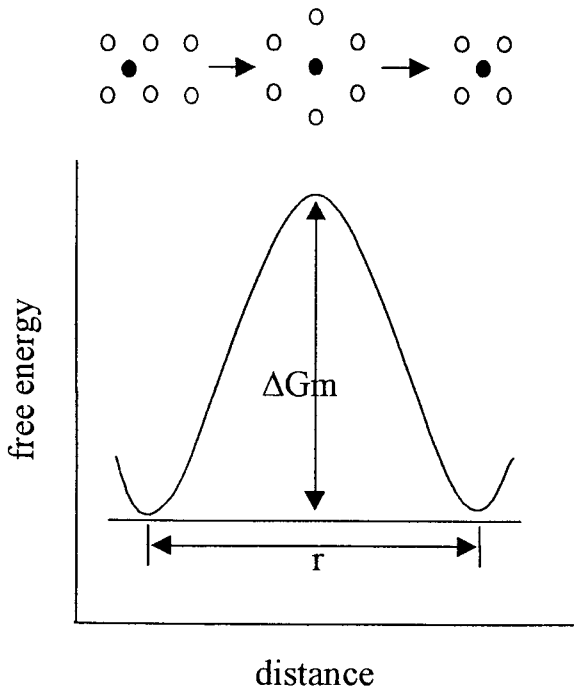

Fig. 6. Spatial energy variation during the diffusion of ions

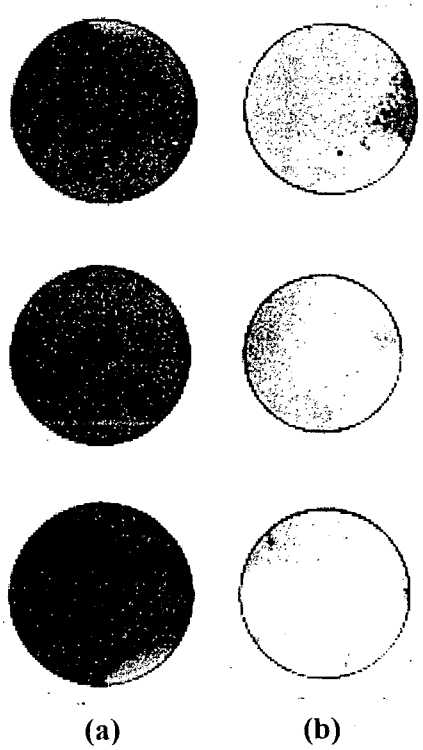

Fig. 7. Cr diffused sapphire (a) unpolished (b) polished