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Effect of Seed Crystal on Zirconium Oxide Formation From Aqueous Solution

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Effect of seed crystal on the formation of ZrO_2 from aqueous solution was investigated. A glass substrate was soaked in Na_2ZrF_6 and H_3BO_3 mixed aqueous solution for 3 d with or without ZrO_2 seed crystals. Without seed crystal, no ZrO_2 was formed on the substrate. With seed crystals, ZrO_2 formation was observed and the XRD peak intensity increased with increasing amount of seed crystals in the mixed solution. This indicates that the seed crystal is indispensable for ZrO_2 formation from Na_2ZrF_6 and H_3BO_3 mixed aqueous solution. Ultrasonic vibration for suitable period enhanced the formation of ZrO_2. Growth and connection of ZrO_2 particles were observed in SEM micrograph on the substrate.
Key words: Zirconium oxide, Aqueous solution, Seed crystal, Fluoro complex

1. INTRODUCTION

Zirconium oxide (ZrO_2) has been used as a functional material with wide range of application. ZrO_2 is a candidate of gate insulator material with high dielectric constant replacing presently used silicon dioxide in the next generation of MOS-FET [1]. ZrO_2 also has a potential application as a biomaterial because it has an ability to induce formation of bone-like high biocompatible hydroxyapatite [2]. Also, zirconium oxide solid solutions have high oxide ion conductivity and used for oxygen sensor, solid oxide fuel cell (SOFC), oxygen separation membrane and so on [3]. For the practical application of ZrO_2, technique for thin film formation is important.

ZrO_2 thin film was prepared by sol-gel process [4] or vapor phase process such as chemical vapor deposition [5], sputtering [6] and so on. However, these methods have several disadvantages. Sol-gel process, and chemical vapor deposition require heating, which is injurious because of the possibility of a change in the shape and/or size of the film and of crack formation, and are not applicable for low heat resistant substrates. For sputtering, expensive vacuum equipments are required and the film areas are restricted.

Recently, we have presented methods for forming oxide ceramics from aqueous solution [7-10]. ZrO_2 can be formed from aqueous solution at ordinary temperature and ordinary pressure by hydrolysis reaction of zirconium fluoro-complex [7]. This method is advantageous because no vacuum, no high temperature and no expensive apparatus will be required, and substrates, even those with wide areas and/or complicated shapes, are available. The reaction mechanism is considered as follows. The chemical equilibrium between hexafluorozirconate ion and ZrO_2 holds as in reaction (1)

$$ZrF_6^{2-} + 2H_2O \rightleftarrows ZrO_2 + 6F^- + 4H^+. \quad (1)$$

When borate ion is added, fluoride ion is consumed by reaction (2)

$$BO_3^{3-} + 4F^- + 6H^+ \rightarrow BF_4^- + 3H_2O. \quad (2)$$

Then the chemical equilibrium in reaction (1) is shifted from left to right in order to increase fluoride ions, resulting in the formation of ZrO_2.

In the present study, the effect of seed crystal on the formation of ZrO_2 from aqueous solution by hydrolysis reaction of zirconium fluoro-complex was investigated.

2. EXPERIMENTAL

2.1 Preparation of ZrO_2 seed crystal

ZrO_2 powder and distilled water were mixed and left to stand for 1 week. Then supernatant liquid was collected at 20 mm depth from the surface of the water by a pipette. Thus obtained ZrO_2 nano particles were used as seed crystal. ZrO_2 content of the collected supernatant liquid was measured as 5.5×10^{-4} mol·dm^{-3} by a gravimetric method. The diameter of ZrO_2 particles in the collected supernatant was estimated to be less than 110 nm from Stokes' law as equation (3)

$$d = 2\sqrt{\frac{9\eta h}{2(\rho-\rho_0)gt}}. \quad (3)$$

d: diameter of ZrO_2 nano particle
h: sedimentation distance (=2.0×10^{-2} m)
t: sedimentation time (=1 w=604800 s)
ρ: density of particle (=5.68×10^3 kg·m^{-3})
ρ_0: density of medium (=0.998×10^3 kg·m^{-3})
η: coefficient of viscosity of medium (=0.001 kg·s^{-1}·m^{-1})
g: gravitational acceleration (9.80 m·s^{-2})

2.2 Formation of ZrO_2

Commercial soda-lime slide glass was cut to 10 × 15 × 1 mm^3 in size and used as a substrate. Prescribed amount of Na_2ZrF_6 was dissolved in 10 cm^3 of distilled water. Prescribed amount of H_3BO_3 was dissolved in 30 cm^3 of distilled water in which various amount of ZrO_2 nano particle mentioned above was added as seed crystal.

Na_2ZrF_6 solution was mixed with thus prepared H_3BO_3 solution in a plastic bottle. The concentration of Na_2ZrF_6 in the mixed solutions was 9.4 mmol·dm^{-3} and the concentration of H_3BO_3 was 28.2 mmol·dm^{-3}. The concentrations of ZrO_2 seed crystals were varied as 0, 1.4×10^{-5}, 6.9×10^{-5}, 9.6×10^{-5} or 1.4×10^{-4} mol·dm^{-3}. The substrate was suspended in the mixed solution. Ultrasonic vibration was applied for 0 to 20 min immediately after the soak of the substrate. Then the solution was allowed to be placed in an incubator at 30°C for 3 d. After soaking, the substrate was washed with distilled water and dried at room temperature. No heat treatment was conducted.

2.3 Analysis

The surface of the substrate after soaking was analyzed by thin film X-ray diffraction (TF-XRD: Rint 2500, Rigaku, Japan) and scanning electron microscopy (SEM: ESEM-2700, Nicon, Japan) to investigate the formation of ZrO_2. Change of particle size distribution of ZrO_2 seed crystal due to ultrasonic vibration was analyzed by particle size distribution analyzer (LA-700, HORIBA, Japan).

3. RESULTS AND DISCUSSION

Figure 1 shows TF-XRD patterns of surface of the substrate before and after soaking in Na_2ZrF_6 and H_3BO_3 mixed solution without seed crystal. Without seed crystal, no XRD peak attributed to ZrO_2 was observed and only halo attributed to glass substrate was observed. No deposition of ZrO_2 was also confirmed by SEM observation. This indicates that ZrO_2 was not formed from Na_2ZrF_6 and H_3BO_3 mixed solution without seed crystal. Figure 2 to 5 show TF-XRD patterns of surface of the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with various amount of seed crystal and ultrasonic vibration for various periods. TF-XRD pattern of substrate before soaking was also given as a reference. XRD peaks attributed to ZrO_2 was observed for all samples except for the case of 1.4×10^{-5} mol·dm^{-3} seed crystal and 0 min ultrasonic vibration. However the determination of the peak existence is very subtle for this case. Among the samples with 0 min ultrasonic vibration, the peak intensity was correlated with the amount of seed crystal as almost nothing for the sample with 1.4×10^{-5} mol·dm^{-3} seed crystal and maximum for the sample with 1.4×10^{-4} mol·dm^{-3} seed crystal. It is clear that seed crystal is effective for the formation of ZrO_2 from Na_2ZrF_6 and H_3BO_3 mixed solution. And taking into consideration of the result that no ZrO_2 was formed without seed crystal, it can be said that seed crystal is indispensable to the formation of ZrO_2 from Na_2ZrF_6 and H_3BO_3 mixed solution. For the cases of 1.4×10^{-5} mol·dm^{-3} seed crystal, 6.9×10^{-5} mol·dm^{-3} seed crystal and 9.6×10^{-5} mol·dm^{-3} seed crystal, the XRD peak intensity increased with the increase of the period of ultrasonic vibration. It is considered that seed crystals were dispersed by ultrasonic vibration and ZrO_2 formation was enhanced. For the case of 1.4×10^{-4} mol·dm^{-3} seed crystal, the peak intensity was maximal with 10 min ultrasonic vibration, but decreased with longer ultrasonic vibration contrary to the other case. These tendency were also indicated in Fig. 6, which shows intensity of ZrO_2 main peak versus the period of

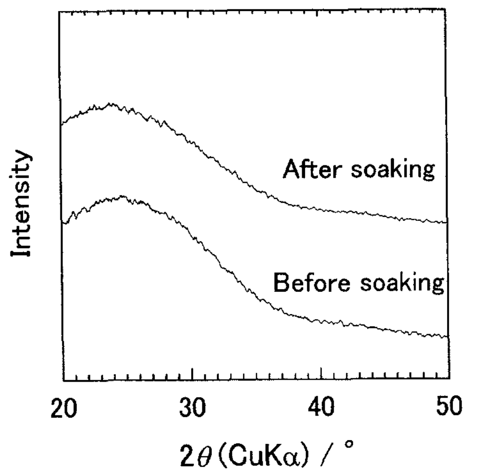

Fig. 1 TF-XRD patterns of surface of the substrate before and after soaking in Na_2ZrF_6 and H_3BO_3 mixed solution without seed crystal.

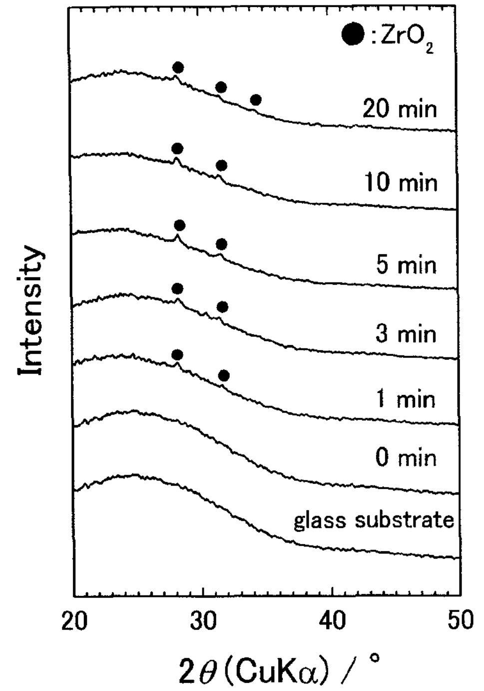

Fig. 2 TF-XRD patterns of surface of the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with 1.4×10^{-5} mol·dm^{-3} seed crystal and ultrasonic vibration for various periods. TF-XRD pattern of substrate before soaking was also given as a reference.

ultrasonic vibration. It is considered that application of ultrasonic vibration for excessively long period will rather agglomerate seed crystal and reduced the effectiveness when larger amount of seed crystal is added.

The influence of ultrasonic vibration on the particle size of seed crystal was measured by particle size distribution analyzer. The concentration of ZrO_2 seed crystal was set to 5.5×10^{-4} mol·dm^{-3}, which is higher

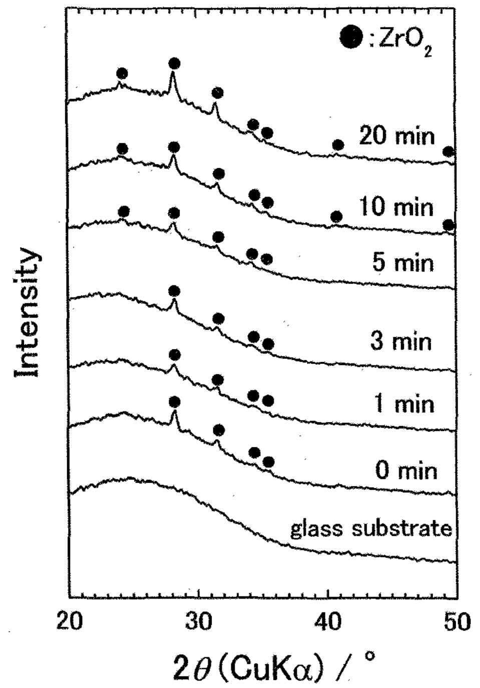

Fig. 3 TF-XRD patterns of surface of the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with 6.9×10^{-5} mol·dm^{-3} seed crystal and ultrasonic vibration for various periods. TF-XRD pattern of substrate before soaking was also given as a reference.

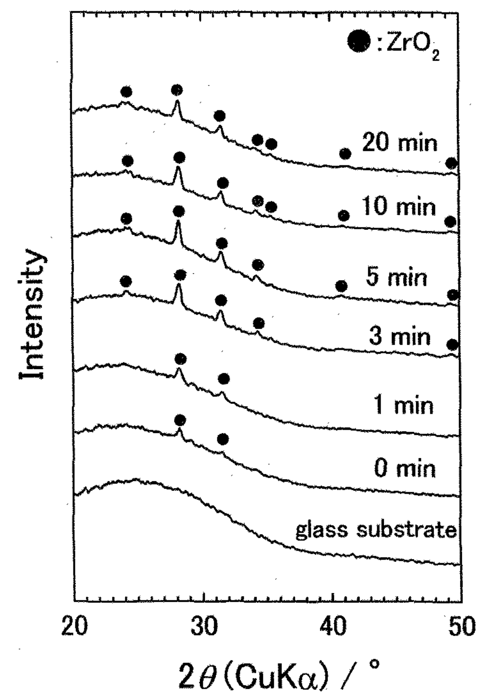

Fig. 4 TF-XRD patterns of surface of the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with 9.6×10^{-5} mol·dm^{-3} seed crystal and ultrasonic vibration for various periods. TF-XRD pattern of substrate before soaking was also given as a reference.

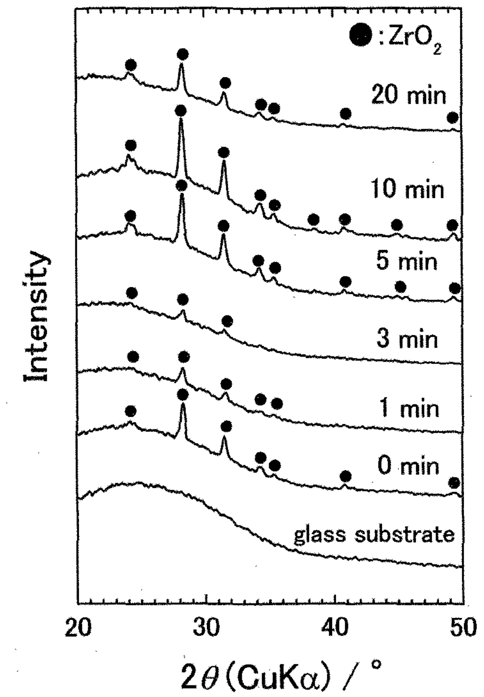

Fig. 5 TF-XRD patterns of surface of the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with 1.4×10^{-4} mol·dm^{-3} seed crystal and ultrasonic vibration for various periods. TF-XRD pattern of substrate before soaking was also given as a reference.

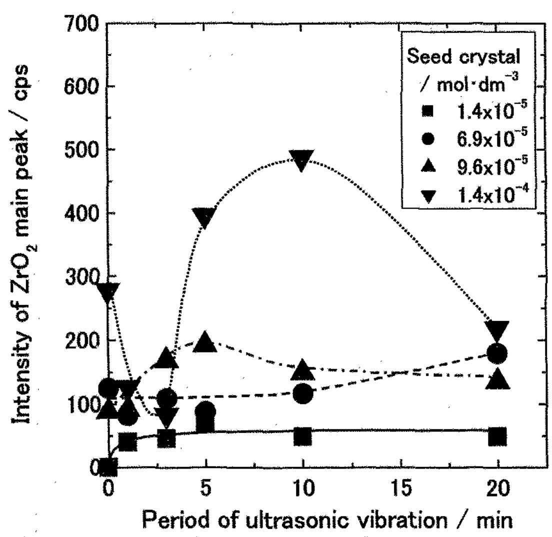

Fig. 6 Intensity of ZrO_2 main peak versus period of ultrasonic vibration.

than that in any of the Na_2ZrF_6 and H_3BO_3 mixed solutions, however these were not high enough for the measurement. Figure 7 shows particle size distribution of ZrO_2 seed crystal with ultrasonic vibration for 1 or 10 min. Without ultrasonic vibration, particle size distribution of ZrO_2 seed crystal could not be measured, maybe the particle size was less than the detection limit of the equipment. After 1 min ultrasonic vibration, the particle size distribution of ZrO_2 seed crystal showed

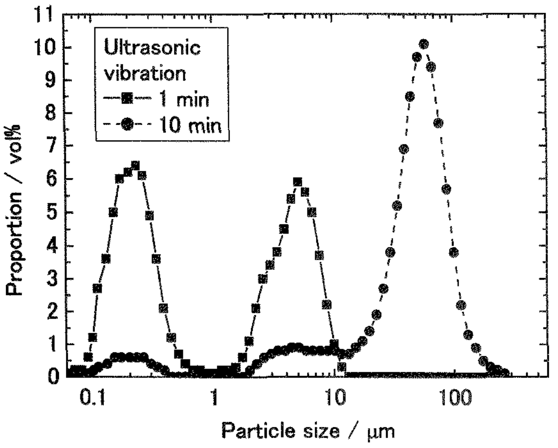

Fig. 7 Particle size distribution of ZrO_2 seed crystal in as-prepared supernatant liquid with ultrasonic vibration for 1 or 10 min

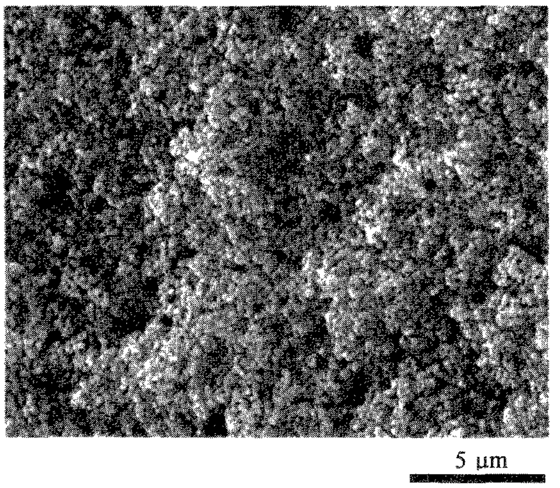

Fig. 8 SEM micrograph of the the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with 1.4×10^{-4} $mol\cdot dm^{-3}$ seed crystal and ultrasonic treatment for 10 min.

two peaks at around 0.2 μm and 5 μm. This indicates that ZrO_2 seed crystal was already agglomerated after 1 min ultrasonic vibration. After 10 min ultrasonic vibration, the peaks at around 0.2 μm and 5 μm almost disappeared and another new peak at around 60 μm was observed. This indicates that agglomeration of ZrO_2 seed crystal proceeded with the increase of period of ultrasonic vibration. Though the concentration is higher, it is considered that similar aggregation phenomenon occurred in the mixed solution.

Figure 8 shows SEM micrograph of the surface of the substrate soaked in Na_2ZrF_6 and H_3BO_3 mixed solution with 1.4×10^{-4} $mol\cdot dm^{-3}$ seed crystal and ultrasonic vibration for 10 min. It is seen that ZrO_2 particles around 200 nm in diameter were deposited all over the surface of the substrate. ZrO_2 particles are observed gathering, growing and connecting with each other to form film-like aggregates.

4. CONCLUSIONS

The effect of seed crystal on the formation of ZrO_2 from Na_2ZrF_6 and H_3BO_3 mixed aqueous solution was investigated. Without seed crystal, ZrO_2 formation was not observed. When seed crystals were added to the Na_2ZrF_6 and H_3BO_3 mixed aqueous solution, ZrO_2 formation was observed and the XRD peak intensity of ZrO_2 increased with the increase of seed crystal amount. It is indicated that the seed crystal is indispensable to the formation of ZrO_2 from Na_2ZrF_6 and H_3BO_3 mixed aqueous solution. Application of ultrasonic vibration immediately after the soak of the substrate enhanced the formation of ZrO_2, however, application of ultrasonic vibration for excessively long period rather reduced the effectiveness when larger amount of seed crystal was added. In SEM micrograph on the substrate, particles are observed gathering, growing and connecting with each other to form film-like aggregates.

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