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Effect of hydrothermal process for inorganic alumina sol on crystal structure of alumina gel

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ABSTRACT

This paper reports the effect of a hydrothermal process for alumina sol on the crystal structure of alumina gel derived from hydrothermally treated alumina sol to help push forward the development of low temperature synthesis of α-Al_2O_3. White precipitate of aluminum hydroxide was prepared with a homogeneous precipitation method using aluminum nitrate and urea in aqueous solution. The obtained aluminum hydroxide precipitate was peptized by using acetic acid at room temperature, which resulted in the production of a transparent alumina sol. The alumina sol was treated with a hydrothermal process and transformed into an alumina gel film by drying at room temperature. Crystallization of the alumina gel to α-Al_2O_3 with 900 °C annealing was dominant for a hydrothermal temperature of 100 °C and a hydrothermal time of 60 min, as production of diaspore-like species was promoted with the hydrothermal temperature and time. Excess treatments with hydrothermal processes at higher hydrothermal temperature for longer hydrothermal time prevented the alumina gel from being crystallized to α-Al_2O_3 because the excess hydrothermal treatments promoted production of boehmite.

1. Introduction

Both electro-conductive materials such as gold, silver, and copper and electro-insulative materials such as plastics and glass are essential for producing electronic devices such as printed circuits [1–4]. Alumina has excellent properties in thermal conductivity and electrical insulation and is inexpensive. These features are utilized for practical electronic devices [5–7].

There are various crystal structures in alumina, the most electro-insulative of which is α-Al_2O_3. α-Al_2O_3 has been conventionally obtained by producing aluminum hydroxide with a liquid phase method using aluminum salts or minerals and annealing the aluminum hydroxide at temperatures of 1000 °C and higher [8–12]. Several researchers have proposed a sol–gel method, which is another representative liquid phase technique, as a candidate for fabricating α-Al_2O_3 [13–15]. Since the sol–gel method is a low temperature synthesis method that does not require large-scale equipment, and it is easy to attain homogeneous compositions, it is a good candidate for a future process. In all the methods mentioned above, the as-prepared materials are required to be annealed at high temperature to transform them into α-Al_2O_3. However, low temperature processes for producing α-Al_2O_3 are desired for saving energy and reducing thermal load on the electronic devices during fabrication. In a previous work, we demonstrated that seeding α-Al_2O_3 nanocrystallites into alumina lowered the annealing temperature for crystallization of the alumina to α-Al_2O_3 [16,17]. There was a risk, though, that the alumina might become inhomogeneous with the seeding, which deteriorates its function. Gas phase techniques such as chemical vapor deposition and sputtering can also be used for fabricating α-Al_2O_3 [18–21]. These techniques are limited to the production of films on substrate and require large-scale and high-cost equipment operated in vacuum, which is disadvantageous from a practical viewpoint.

Most sol–gel methods for fabricating alumina typically use aluminum alkoxide as a starting material [13–15]. Our research group has also studied the fabrication of alumina with a sol–gel method using aluminum alkoxide [20]. The main difficulty with using alkoxide arises from its high cost. Another difficulty is that alcohol produced with the hydrolysis of the alkoxide remains in the final materials, which also deteriorates the function. Bearing this in

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mind, our group proposed a method for producing alumina with the use of aluminum salt [22], which is much less expensive than alkoxide. Aluminum hydroxide was prepared with a homogeneous precipitation method using aluminum nitrate and urea in aqueous solution, and alumina sol was obtained by peptizing with acetic acid at room temperature (inorganic alumina sol). However, alumina gel produced from the inorganic alumina sol could not be crystallized to α-Al_2O_3 by annealing at 900 °C.

The hydrothermal process for materials in water promotes crystal growth of the materials. Various researchers have reported that crystallization and crystal growth of material are influenced by the hydrothermal process [23–27]. It makes sense then that the hydrothermal process for alumina sol may promote crystallization of alumina to α-Al_2O_3 and its crystal growth. The purpose of the present work is to study the effects of the hydrothermal process for our inorganic alumina sol on the crystallinity of alumina gel, which should be useful for the development of a low temperature method for producing α-Al_2O_3.

2. Experimental

2.1. Chemicals

The starting material for aluminum hydroxide and the precipitation-inducer for preparing the aluminum hydroxide were aluminum nitrate enneahydrate ($Al(NO_3)_3{\cdot}9H_2O$) (98.0%) and urea (99.0%), respectively. The peptizer for aluminum hydroxide was acetic acid (99.7%). All chemicals were purchased from Kanto Chemical Co., Inc. and were used as received. Water that was ion-exchanged and distilled with a Yamato WG-250 was used in all preparations.

2.2. Preparation

The inorganic alumina sol was prepared in accordance with our previous work [22]. The homogeneous precipitation method was then used for producing precipitate of aluminum hydroxide, as follows. An aqueous solution dissolving the $Al(NO_3)_3$ and the urea at initial concentrations of 0.2 and 5 M, respectively, was stirred in a hermetically sealed glass bottle at 80 °C for 8 h, which produced white precipitate. The precipitate was aged at room temperature for 12 h and washed by repeating a process of centrifugation, removal of supernatant, addition of water, and sonication three times or more. The acetic acid was added to the washed precipitate at 25 °C (room temperature) to peptize the precipitate, in which the molar ratio of [acetic acid]/[Al^{3+}] was 0.15. With the peptization process, the precipitate was transformed to a transparent sol in ca. 12 h after the addition of acetic acid. The transparent sol was termed 'precursor alumina sol'. The precursor alumina sol was treated with a hydrothermal process at 60–160 °C (hydrothermal temperature) for 20–120 min (hydrothermal time) in a Teflon-lined stainless steel autoclave. The hydrothermally treated sol was termed 'hydrothermal alumina sol'. The precursor alumina sol and the hydrothermal alumina sol were cast onto a Petri dish. Drying in air at room temperature converted the sols into solid alumina gels, termed 'precursor alumina gel' and 'hydrothermal alumina gel', respectively. The solid gel was pulverized with a mortar into powder and then annealed in air at 900 °C with a Yamato FO100 muffle furnace. The temperature was increased up to the target annealing temperature at a temperature raising rate of 10 °C/min.

2.3. Characterization

The gels were characterized by X-ray diffractometry (XRD). Samples for XRD measurements were powders obtained by pulverizing alumina gel with a mortar. The XRD measurements were carried out with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with Cu Kα_1 radiation. The two main types of crystal structures in Al_2O_3 are α and γ. The crystallinity of alumina gel was studied using their XRD intensities. One of the XRD peaks due to α-Al_2O_3 and γ-Al_2O_3 is detected at 43.4 and 45.8 degrees, respectively. Since these peaks are far apart, that is, they are not overlapped, they were used for the study on crystallinity. XRD intensity ratio of α-Al_2O_3/γ-Al_2O_3 was defined as the peak intensity (counts per second (cps)) of α-Al_2O_3 at ca. 43–44 degrees divided by that of γ-Al_2O_3 at ca. 45–46 degrees. The ratio for neither the detection of the XRD peak of α-Al_2O_3 nor that of γ-Al_2O_3 was considered as zero.

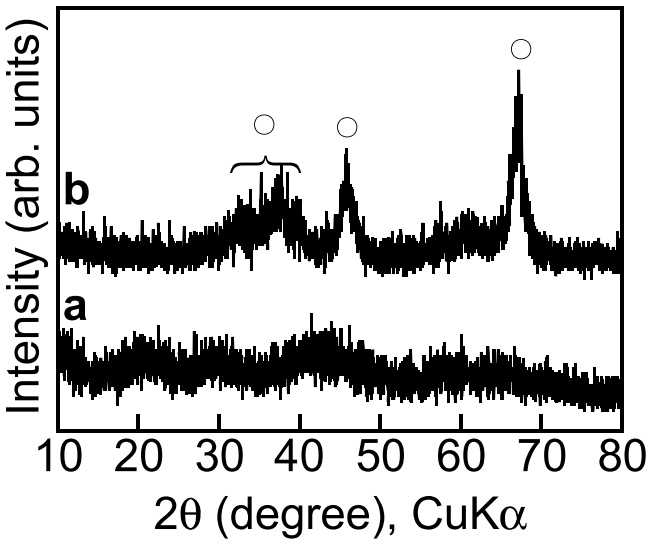

Fig. 1. XRD patterns of precursor alumina gels. Samples were (a) as-prepared precursor alumina gel and (b) precursor alumina gel annealed at 900 °C. ○: γ-Al_2O_3.

3. Results and discussion

3.1. Precursor alumina gel

Fig. 1 shows XRD patterns of precursor alumina gels. Since the pattern for as-prepared precursor alumina gel was broad, the gel was more or less amorphous or crystallites that were too fine to be detected. After annealing at 900 °C, peaks appeared at 30–40, 45.8, and 67.2 degrees. They were attributed to γ-Al_2O_3 (according to references [28,29] and to a JCPDS card (#29-0063)). This result reveals that transformation from amorphous or poorly crystallized alumina to γ-Al_2O_3 crystallites took place with the annealing. Another noted point is that no α-Al_2O_3 crystallites were produced with the annealing at 900 °C.

3.2. Hydrothermal alumina gel

3.2.1. Effect of annealing temperature

Fig. 2 shows XRD patterns of hydrothermal alumina gels annealed at various temperatures, in which the hydrothermal temperature and time for the precursor sol were 100 °C and 60 min, respectively. A broad pattern was detected for the as-prepared alumina gel and the alumina gels annealed at 500 and 600 °C, which indicates that the as-prepared alumina gel was stable in the states such as amorphous or fine crystallite even for annealing at a temperature of 600 °C. For 700 and 800 °C, peaks attributed to γ-Al_2O_3 appeared at 30–40, 46.0, and 66.9 degrees. This result reveals that transformation from amorphous or poorly crystallized alumina to γ-Al_2O_3 crystallite took place with the annealing at 700 °C, and no α-Al_2O_3 crystallite was produced with the annealing at 800 °C.