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Research Article

Low Temperature Synthesis of α-Alumina with a Seeding Technique

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This paper reports a method for producing α-Al_2O_3 at low temperature, which uses a seeding technique. White precipitate of aluminum hydroxide, which was prepared with a homogeneous precipitation method using aluminum nitrate and urea in aqueous solution, was peptized by using acetic acid at room temperature and then transformed to a transparent alumina sol. To the alumina sol α-Al_2O_3 particles were added as a seed, and then the sol containing α-Al_2O_3 particles was transformed to an α-Al_2O_3-seeded alumina gel by drying the sol at room temperature. The nonseeded alumina gel was amorphous or fine crystallites even after being annealed at 600°C and was crystallized to γ-Al_2O_3 at 700°C. The α-Al_2O_3 seeding promoted crystallization of alumina gel to α-Al_2O_3. The promotion of crystallization was made remarkable with a decrease in α-Al_2O_3 particle size and an increase in α-Al_2O_3 particle content in weight for the final seeded alumina gel. With an α-Al_2O_3 particle size of 150 nm and an α-Al_2O_3 particle content of 5%, the seeded alumina gel was partially crystallized to α-Al_2O_3 by annealing at a temperature as low as 700°C and mostly at 900°C.

1. Introduction

Not only electroconductive materials such as gold, silver, and copper but also electric-insulating materials are quite essential for producing electronic devices such as integrated circuits [1–3]. Alumina is one of representative electric-insulating materials. Since it has high thermal conductivity and high chemical stability at high temperature compared to other electro-insulating materials such as glass, plastic, and paper [4–6], it is promising as the electric-insulating material used in the electronic devices.

There are various crystal structures in the alumina. Among the various crystal structures, alumina that reveals electric insulation is of α type. The α-alumina has been conventionally produced by annealing aluminum hydroxide derived from aluminum salts or minerals at temperatures higher than 1000°C [7–10]. The α-alumina can be also produced by fabricating amorphous alumina with methods using liquid phase such as precipitation and sol-gel process and then annealing it at high temperature [11–13]. These methods need the high temperatures, which brings about much consumption of energy. Accordingly, low temperature processes for producing α-alumina are desired for saving energy.

Our research group has studied effects of nanocrystallites seeding on various titanates such as PZT and BST fabricated by the sol-gel method for the last decade [14–17]. As a result, their crystallization temperatures were lowered with the seeding. The titanates were epitaxially crystallized on surface of the crystallites, which provided the lowering of crystallization temperatures, though its mechanism is still unclear. Accordingly, the crystallization temperature of alumina, that is, the temperature for transformation of amorphous alumina to α-alumina, is likely to be also lowered with the seeding technique.

Our previous work proposed methods for preparing alumina sol by utilizing a homogeneous precipitation method and for fabricating transparent alumina films [18]. Since the method used aluminum salt and did not need heating for peptization of aluminum hydroxide precipitate, cost and energy for the fabrication of alumina could be saved.

The obtained alumina film was amorphous or fine crystallites even after being annealed at a temperature as high as 500°C and was crystallized to γ-Al_2O_3 at 900°C, which implied that the alumina was required to be annealed at further higher temperatures for transformation to α-Al_2O_3.

The aim of the present work is to study the effect of α-alumina seeding on crystallization of alumina fabricated with our previous alumina and to lower annealing temperature for production of α-Al_2O_3.

2. Materials and Methods

2.1. Materials. Aluminum nitrate enneahydrate ($Al(NO_3)_3 \cdot 9H_2O$) (98.0%) and urea (99.0%) were used as starting material for aluminum hydroxide and a precipitation inducer for preparation of aluminum hydroxide, respectively. Acetic acid (99.7%) was used as a peptizer for aluminum hydroxide. Two kinds of α-Al_2O_3 particles were used as seed crystallines, namely, α-Al_2O_3 (nanoalumina) (99.85%, Ionic Liquids Technologies) and α-Al_2O_3 (microalumina) (99.0%). According to their data in catalogue, they have particle sizes of 150 nm and 35–50 μm, respectively. Except for the nanoalumina, all chemicals were purchased from Kanto Chemical Co., Inc., and were used as received. Water that was ion-exchanged and distilled with Yamato WG-250 was used in all the preparations.

2.2. Methods

2.2.1. Preparation. Precipitate of aluminum hydroxide was prepared by the homogeneous precipitation method or by the following procedure. The $Al(NO_3)_3$ and the urea were dissolved in water in a hermetically sealed glass bottle at initial concentrations of 0.2 M $Al(NO_3)_3$ and 5 M urea. The mixture was stirred at 80°C for 8 h, which produced white precipitate. The obtained precipitate was aged at room temperature for 12 h after the preparation, washed by repeating centrifugation, removal of supernatant, addition of the water, and sonication over three times, and then peptized at 25°C (room temperature) with the addition of acetic acid at $[acid]/[Al^{3+}]$ molar ratios of 0.15. The precipitate was transformed to a transparent sol (alumina sol) in ca. 12 h after the peptization. The α-Al_2O_3 particles were dispersed in the sol at 1–5% in weight for final alumina gel seeded with the α-Al_2O_3 particles. Then, the sol containing the particles was casted onto a petri dish. Drying in air at room temperature converted the sol into a solid alumina gel. The solid gel was pulverized with a mortar into powder and then annealed in air at various temperatures.

2.2.2. Characterization. Actual Al concentrations in particle colloid solutions were measured by inductively coupled plasma (ICP) emission spectroscopy. ICP measurement was performed with a Shimadzu ICPS-7510 atom emission spectrometer. Emission was detected at a wavelength of 396.153 nm. Samples for ICP were prepared by dissolving the particles with aqua regia completely and then diluting the obtained solution with water to adjust its concentrations to concentrations suitable for the measurements.

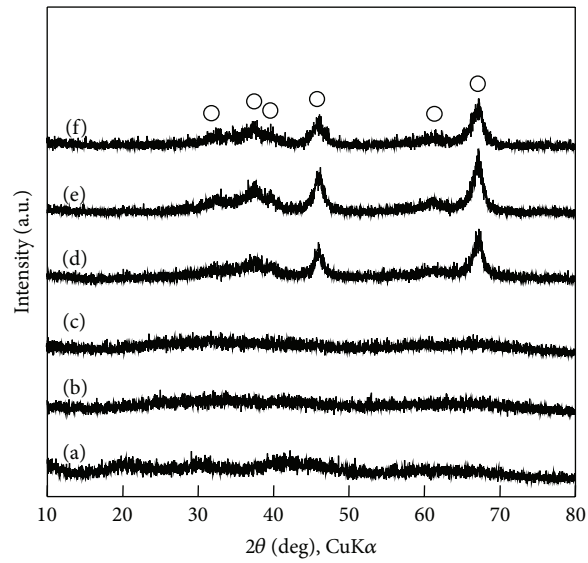

Figure 1: XRD patterns of nonseeded alumina gels. Sample (a) is as-prepared alumina. Samples (b), (c), (d), (e), and (f) were alumina gels annealed at 500, 600, 700, 800, and 900°C, respectively. ○: γ-Al_2O_3.

The gels were characterized by X-ray diffractometry (XRD) and thermal analysis (TG-DTA). Powder, which was obtained by pulverizing alumina gel with a mortar, was used as samples for XRD measurements. The XRD measurements were carried out with a Rigaku Ultima IV X-ray diffractometer at 40 kV and 30 mA with CuKα_1 radiation. There are mainly two types in crystal structures of Al_2O_3: α and γ. Their XRD intensities were compared to study on crystallinity of alumina gel. α-Al_2O_3 and γ-Al_2O_3 reveal XRD peaks at 43.4 and 45.8 degrees that are not overlapped, respectively. 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 43.4 degree divided by that of γ-Al_2O_3 at 45.8 degree. When neither the XRD peak of α-Al_2O_3 nor that of γ-Al_2O_3 was detected, the ratio was considered as zero. TG-DTA was performed in air at a heating rate of 10°C/min with a Rigaku Thermo plus EVO TG8120 thermal analyzer. Samples for TG-DTA measurements were obtained in the same manner as that for the XRD samples.

3. Results and Discussion

3.1. Alumina Gels. The ICP measurement showed that an Al concentration in the sol was 0.717 M, which indicated that 71.0% of the $Al(NO_3)_3$ was transformed to the alumina sol. According to our previous work, the as-prepared gel obtained from the sol was transparent. Figure 1 shows XRD patterns of alumina gels annealed at various temperatures. A few peaks were detected around 20, 30, and 40 degrees in the as-prepared alumina gel. They were roughly assigned to those of pseudoboehmite, according to the reference [19]. Since these peaks were broad and diffuse, the as-prepared gel was amorphous or fine crystallites. No dominant peaks

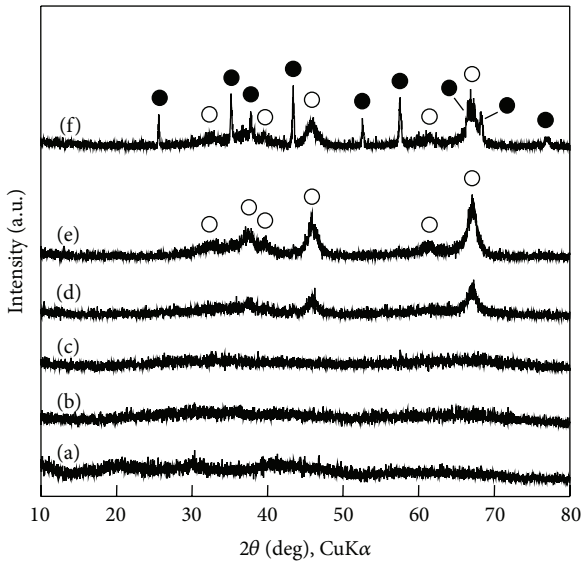

Figure 2: XRD patterns of alumina gels seeded with 1% microalumina. Sample (a) is as-prepared alumina. Samples (b), (c), (d), (e), and (f) were alumina gels annealed at 500, 600, 700, 800, and 900°C, respectively. ●: α-Al_2O_3, ○: γ-Al_2O_3.

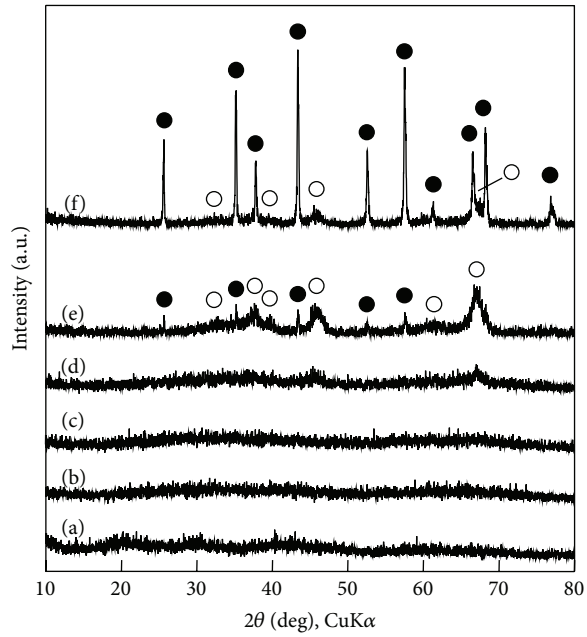

Figure 3: XRD patterns of alumina gels seeded with 1% nanoalumina. Sample (a) is as-prepared alumina. Samples (b), (c), (d), (e), and (f) were alumina gels annealed at 500, 600, 700, 800, and 900°C, respectively. ●: α-Al_2O_3, ○: γ-Al_2O_3.

appeared even for annealing at a temperature as high as 600°C; the alumina was still amorphous or fine crystallites For 700°C, peaks were detected at 45.8 and 66.8 degrees. They were probably attributed to γ-Al_2O_3 (JCPDS card number 29-0063), which indicated that transformation from poorly crystallized pseudoboehmite to γ-Al_2O_3 began at 700°C. Peaks due to γ-Al_2O_3 other than the two peaks also appeared over 700°C, and they became clearly detected with an increase in annealing temperature. This result indicated that the annealing promoted the crystallization of alumina gel.

3.2. Alumina Gels Seeded with α-Al_2O_3 Particles

3.2.1. Effect of Seeding of α-Al_2O_3 Particles. Figure 2 shows XRD patterns of alumina gels seeded with microalumina particles. For the annealing temperatures of 25 (as prepared) to 800°C, there was no large difference in the XRD patterns between the nonseeded (Figure 1) and the seeded. This indicated that the seeding did not affect crystal structure of alumina gel in the range of annealing temperatures from 25 to 800°C. For 900°C, peaks were detected at 25.6, 35.2, 43.4, 52.6, and 57.5 degrees besides the peaks of γ-Al_2O_3. They were attributed to α-Al_2O_3 (JCPDS card number 42-1468). The nonseeded alumina gel annealed at 900°C revealed no α-Al_2O_3 peaks, as shown in Figure 1(f). Accordingly, the crystallization of alumina gel to α-Al_2O_3 was effected by the seeding. The alumina gel was probably crystallized epitaxially on α-Al_2O_3 particle surface.

3.2.2. Effect of α-Al_2O_3 Particle Size. Figure 3 shows XRD patterns of alumina gels seeded with nanoalumina particles. For the annealing temperatures of 25 (as prepared) to 700°C, there were no large differences in the XRD patterns among the nonseeded alumina gel (patterns (a)–(d) in Figure 1), the alumina gel seeded with microalumina particles (patterns (a)–(d) in Figure 2), and the alumina seeded with nanoalumina particles (patterns (a)–(d) in Figure 3). For 800°C, peaks due to α-Al_2O_3 were detected at 25.6, 35.2, 43.4, 52.6, and 57.5 degrees besides the peaks of γ-Al_2O_3. No α-Al_2O_3 peaks appeared in the microalumina-seeded alumina annealed at 800°C (Figure 2(f)). This indicated that a seeding effect of the small α-Al_2O_3 particles on crystallization was dominant compared to the large α-Al_2O_3 particles. A raise of annealing temperature to 900°C provided that most outstanding peaks were attributed to α-Al_2O_3.

Figure 4 shows XRD intensity ratio of α-Al_2O_3/γ-Al_2O_3 plotted as a function of annealing temperature. The plot of the nonseeded alumina was also shown. Since the nonseeded alumina was not crystallized to α-Al_2O_3, the intensity ratio was 0 in the whole range of annealing temperature examined. For the micro-alumina particles, the ratio was 0 at 25–800°C, and increased faintly to 0.39 at 900°C. In contrast, the ratio started to increase at 800°C and reached 3.19 at 900°C.

A total apparent surface area of α-Al_2O_3 particles with a small size is larger than that with a large size at the same amount of α-Al_2O_3 particles. The large surface area of nanoalumina particles provided effective epitaxial crystallization, compared to the small area. Consequently, the crystallization to α-Al_2O_3 was remarkably promoted with the seeding of nanoalumina particles.

3.2.3. Effect of α-Al_2O_3 Particle Content. Whereas the content of α-Al_2O_3 particles was 1% in Figure 3, the α-Al_2O_3 content was raised to study an effect of α-Al_2O_3 particle content in

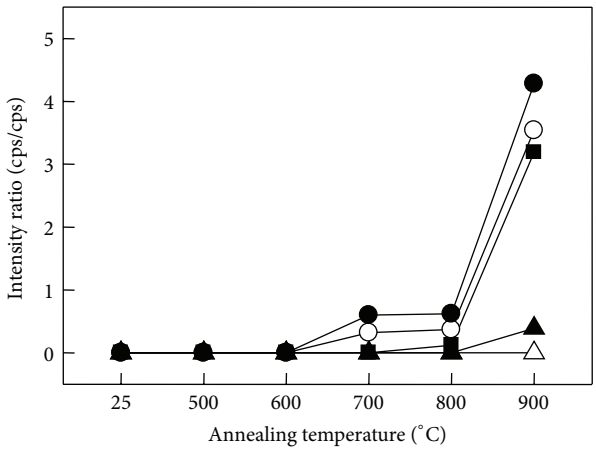

Figure 4: XRD intensity ratios of α-Al_2O_3/γ-Al_2O_3 as a function of annealing temperature. △: nonseeded alumina; ▲: 1% microalumina-seeded alumina; ■: 1% nanoalumina-seeded alumina; ○: 3% nanoalumina-seeded alumina; ●: 5% nanoalumina-seeded alumina.

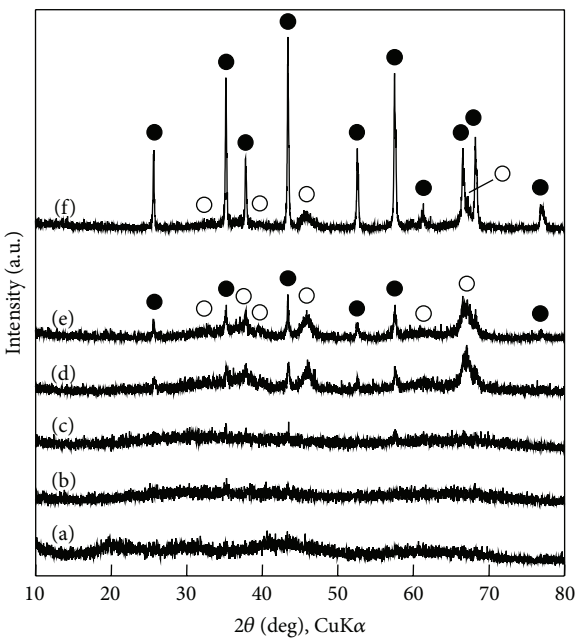

Figure 5: XRD patterns of alumina gels seeded with 3% nanoalumina. Sample (a) is as-prepared alumina. Samples (b), (c), (d), (e), and (f) were alumina gels annealed at 500, 600, 700, 800, and 900°C, respectively. ●: α-Al_2O_3, ○: γ-Al_2O_3.

this section. Figure 5 shows XRD patterns of alumina gels seeded with nanoalumina particles at 3%. For the annealing temperatures of 25 and 500°C, there were no large differences in the XRD patterns between the 1%-nanoalumina-seeded alumina (Figure 3) and the 3%. At 600°C, peaks due to α-Al_2O_3 were faintly observed at 35.2, 43.4, and 57.5 degrees, though not observed for 1%. This indicated that the crystallization to α-Al_2O_3 was more promoted with the increase in α-Al_2O_3 content. These peaks became strong with an increase in annealing temperature. Figure 6 shows XRD patterns of

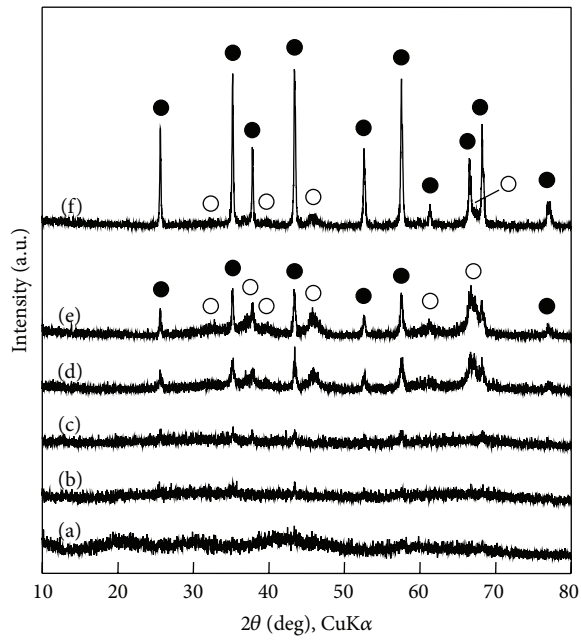

Figure 6: XRD patterns of alumina gels seeded with 5% nanoalumina. Sample (a) is as-prepared alumina. Samples (b), (c), (d), (e), and (f) were alumina gels annealed at 500, 600, 700, 800, and 900°C, respectively. ●: α-Al_2O_3, ○: γ-Al_2O_3.

alumina gels seeded with nanoalumina particles at 5%. The promoted crystallization to α-Al_2O_3, which was observed at 3%, became more dominant with a further increase in α-Al_2O_3 particle to 5%.

XRD intensity ratio of α-Al_2O_3/γ-Al_2O_3 versus annealing temperature was also plotted as shown in Figure 4. The ratios for 3 and 5% started to increase at 700°C, and reached 3.54 and 4.28 at 900°C, respectively.

The large α-Al_2O_3 particle content corresponded to a large apparent surface area of α-Al_2O_3 particles. Accordingly, a mechanism similar to that for the α-Al_2O_3 particle size, which was based on surface area of α-Al_2O_3 particles, was also considered for the effect of α-Al_2O_3 particle content; the large apparent surface area of α-Al_2O_3 particles at the large particle content promoted remarkably the crystallization to α-Al_2O_3.

4. Conclusions

The homogeneous precipitation using aluminum nitrate and urea in aqueous solution was performed for producing the white precipitates of aluminum hydroxide. The transparent alumina sol was successfully produced by the peptization of the aluminum hydroxide with the addition of acetic acid at room temperature. The alumina seeded with α-Al_2O_3 particles was fabricated by drying the sol containing the α-Al_2O_3 particles at room temperature. The nonseeded alumina gel was amorphous or fine crystallites even after being annealed at 600°C and was crystallized to γ-Al_2O_3 by annealing at 700°C. For the alumina seeded with α-Al_2O_3 particles, the crystallization of alumina gel to α-Al_2O_3 was promoted remarkably with a decrease in α-Al_2O_3 particle

size and an increase in α-Al_2O_3 particle content in film. The alumina seeded with the nanoalumina particle size of 150 nm at the α-Al_2O_3 particle content of 5% started to be crystallized to α-Al_2O_3 by annealing at a temperature as low as 700°C.

Conflict of Interests

The nanoalumina and the other chemicals were supplied by Ionic Liquids Technologies and Kanto Chemical, respectively, with no financial support from the two companies.

Acknowledgment

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