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PRODUCTION OF TiO_2 WITH SCRAP COLLECTED BY TRAP IN THE TiN PROCESS

This study synthesized nano-sized TiO_2 using scrap from the TiN thin film manufacturing process by a hydrothermal reaction. By controlling the reaction temperature and concentration, the crystal structure and particle size were controlled. The solution from the TiN scrap was strongly acidic with a pH below 0. The mixed TiO_2 of rutile and anatase crystal structures was produced at a concentration of 0.08 mole. The TiO_2 particle size ranged from 4 nm to 8 nm, increased from 7 nm to 140 nm after heat treatment. At temperatures above 800°C, the crystal structure of the mixed TiO_2 transformed into pure rutile.

Keywords: Nano-sized TiO_2; Hydrothermal reaction; Crystal structure; Particle size

1. Introduction

Semiconductors are classified into memory and non-memory types. Memory includes elements such as capacitors and transistors, while non-memory devices involve arranging 3D transistor structures like MOSFETs on Si wafers [1]. Devices fabricated by semiconductor processes and metal wiring made by metallization connect the power source, enabling electrical flow. Metal wiring is created by various methods. Semiconductor manufacturing involves stacking elements and metal wiring on Si wafers, with a "contact" formed between the element and wiring. Barrier materials are essential between the device and metal wiring. In semiconductor processes, various metals and non-metals are used, and connections between different materials increase resistance and power consumption. Thus, barrier materials are required to reduce power loss. TiN is widely used as a diffusion barrier [2] due to its low electrical conductivity, high melting point, thermal stability, and excellent adhesion [3-6]. In high-density integrated circuits, TiN film formation is crucial but challenging, especially for small and deep holes.

Physical vapor deposition (PVD) is commonly used due to its cleanliness and chemical stability over chemical vapor deposition (CVD). However, for high aspect ratios, PVD often results in overhangs at hole corners [7]. Therefore, CVD TiN films are preferred for their superior step coverage up to aspect ratios of 7 [8]. Various methods have been reported for CVD TiN film manufacturing [9-12], with Tetrakis-dimethylaminotitanium (TDMAT) and Tetrakis-diethylaminotitanium (TDEAT) commonly used. As ultra-high-density circuits developed, atomic layer deposition (ALD) gained attention for forming TiN films. ALD processes require a diffusion barrier layer during heat treatment. In this method, $TiCl_4$ reacts with NH_3 to form a TiN thin layer, with unreacted materials discharged [13]. The discharged $TiCl_4$ and NH_3 are condensed and collected as a solid mixture in a trap, extending facility lifecycles and reducing environmental emissions. The recovered scrap consists only of Ti, N, Cl, and H from high-purity precursors. Although various TiO_2 nanoparticle manufacturing methods have been reported [14], none have utilized scrap from semiconductor manufacturing. Considering the increasing environmental and economic demands in the semiconductor industry, recycling and reusing of used materials, such as TiN process scrap is important. The disposal of this scrap can cause environmental hazards as well as loss of materials. Therefore, the conversion of TiN process scrap into TiO_2 nanoparticles presents an eco-friendly, economical solution and sustainability efforts in semiconductor manufacturing. Thus, this study investigated the synthesis of TiO_2 nanoparticles via hydrothermal reaction, with the solid mixture of $TiCl_4$ and NH_3 recovered from TiN processes, and controlled of the crystal structure and particle size by heat treatment.

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2. Experimental

2.1. Ingredients of base materials

In this study, the scrap generated by the TiN thin film process in semiconductor manufacturing process was used. This scrap was analyzed by SEM-EDS qualitatively and quantitatively.

2.2. Hydrothermal reaction

The hydrothermal reaction process in this study can be explained by dividing it into the following two steps. First, $TiCl_4$ reacts with water to produce TiO_2 and HCl as shown in Eq. (1).

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl \quad (1)$$

2nd step, the resulting HCl reacts with NH_3 to form NH_4Cl as shown in Eq. (2).

$$NH_3 + HCl \rightarrow NH_4Cl \quad (2)$$

When the above two steps are combined, the overall reaction equation can be expressed as Eq. (3).

$$TiCl_4 + 4NH_3 + 2H_2O \rightarrow TiO_2 + 4NH_4Cl \quad (3)$$

When the scrap mixed with $TiCl_4$ and NH_3 is put in water for hydrothermal reaction, TiO_2 and NH_4Cl are formed as final products. In this study, the scrap recoverded from the TiN process was used. The scrap was subjected to a hydrothermal reaction with deionized water (DI water). In hydrothermal reaction, Condition I was conducted at temperatures of 25, 40, 60, 80, 100, and 120°C, at 0.056 moles of NH_4Cl contained in the scrap per mole of DI water. Condition II was varied the concentration of NH_4Cl 0.025, 0.035, 0.045, 0.056, 0.065, and 0.08 moles, at 25°C. All hydrothermal reactions were performed at 150 rpm on a hot plate (Misung Scientific, 2020) [15].

2.3. Separation and drying

The reactants produced by the two reaction conditions, was separated into a liquid, $4NH_4Cl$ and a solid phase, TiO_2 by solid-liquid separation. The separated solid, TiO_2 was washed by an ultrasonic cleaner(saehan, 2017) for 3 minutes in adding DI water. Then, the solid and liquid phase were separated by a centrifuge (Hanil Scientific Inc, 1998). The centrifugation was conducted at 3000 RPM for 15 minutes. The washing process was repeated 3 times for the solid. Finally, The washed solid was dried in a dryer at 80°C for 2 hours.

2.4. Analysis

The particle size of the generated sample from the hydrothermal reaction was calculated using the Scherrer equation, based on results obtained by XRD (koreaits, 2023) and confirmed the crystal structure.

2.5. Heat treatment

The generated precipitates from reaction conditions I and II were heat-treated in a tube furnace (AJEON HEATING INDUSTRIAL CO, 2012) to change the crystal structure and control the particle size. The heat treatment temperature range was based on the differential thermal analysis (DTA) results presented by S.J. Kim et al. [11]. The DTA analysis confirmed that the endothermic reaction began around 650°C and occurred at temperatures of 1000°C or higher. Based on this, the heat treatment temperatures were set at 200, 400, 600, 800, and 1000°C, with heating times of 0.5 and 1 hour, respectively. The heating rate increased by 3°C per minute, and the samples were cooled in the air. [16]

3. Results and discussion

The TiN process scrap contains only Ti, O, Cl, and N, because of ultra-high purity, 6N, precursor $TiCl_4$ and reactants NH_3 in the TiN process. These element's contents of the scrap are 20.48 wt.%N, 25.72 wt.%O, 37.60 wt.%Cl, and 16.10 wt.%Ti. Reaction conditions I were carried out for 2 hours at reaction temperatures of 25°C, 40°C, 60°C, 80°C, 100°C, and 120°C based on 0.056 moles of NH_4Cl in 1 mole of DI water. During the hydrothermal reaction, the reaction temperature was adjusted by a hot plate. The acidity of the scrap solution ranged –0.2 to –8.1, and was measured with a pH meter (hanna, 2022. The pH values changed as shown in Fig. 1, with a notable decrease at temperatures of 100°C.

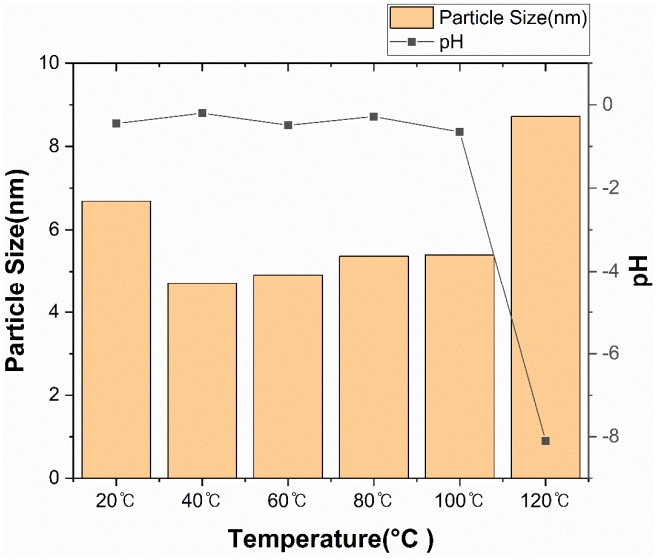

Fig. 1. Variation of particle size and pH under Condition I

The precipitated TiO_2 was subjected to X-ray diffraction (XRD). The particle size of TiO_2 was a nano size. The nano-sized

particles could not be analyzed by a particle size analyzer, so was determined by the Scherrer Eq. (4).

$$D_p = \frac{0.94 \times \lambda}{\beta \times \cos\theta} \quad (4)$$

D_p: Average crystallite size, β: Line broadening in radians, λ: X-ray wavelength, θ: Brag angle.

The particle size analysis was calculated based on the rutile (110) plane. The particle size was 4-9 nm as shown in Fig. 1. The particles grew to less than 6 nm up to 100°C and reached 8.7 nm at 120°C. The crystal structure of TiO_2 was confirmed by X-RD as shown in Fig. 2, the Anatase and Rutile crystal structures were mixed in the entire reaction temperature range. The ratio of Anatase and Rutile is calculated using Eq. (5) [17].

$$X_A = 100/(1 + 1.265\ IR/IA) \quad (5)$$

X_A: Anatase weight fraction in percentage in the TiO_2 powder, IA: anatase (101) intergrated intensity, IR: Rutile (110) intergrated intensity.

As shown in Fig. 3, the ratio of anatase was the lowest 14.83% at 25°C. The ration of anatase, 38.31% was at 120°C. The ratio of Anatase was increased with increasing the reaction temperature, but it decreased to about 23% at 100°C. And the particle size was grown up to the 120°C.

According to the previous report [18], TiO_2 by the sol-gel method with a starting material, titanium tetraisopropoxide (TTIP), have a rutile crystal structure at pH 1. In this study, TiO_2 was produced with a mixture structure of anatase and rutile in a strong acidity of less than pH 0 when TiN process scrap was hydrothermal reaction.

Reaction Condition II, 0.025, 0.035, 0.045, 0.056, 0.065, and 0.08 moles of NH_4Cl contained in TiN scrap were reacted with DI water 1 mole for 2 hours at room temperature (25°C). During the reaction, the temperature of the solution increased due to the heat of the reaction, was between 45-55°C. The acidity of the solution in which the scrap was dissolved, was pH –0.09 to –1.15. the precipitated TiO_2 had rutile crystal structure in reaction condition II, but it had anatase crystal structure at

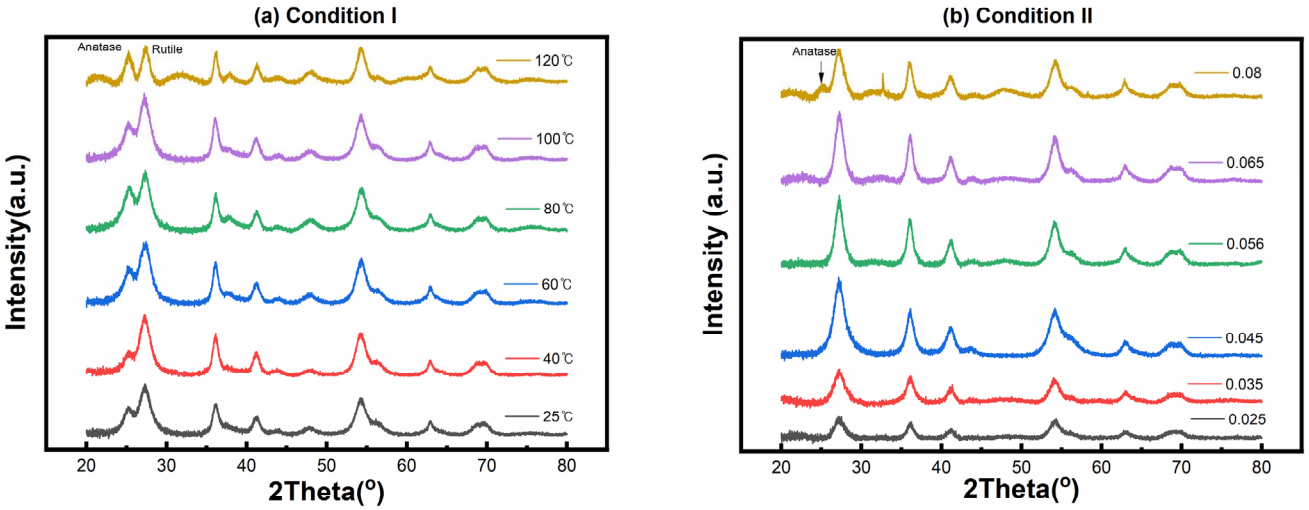

Fig. 2. Comparison of XRD patterns of TiN-derived materials on a) Condition I and b) Condition II

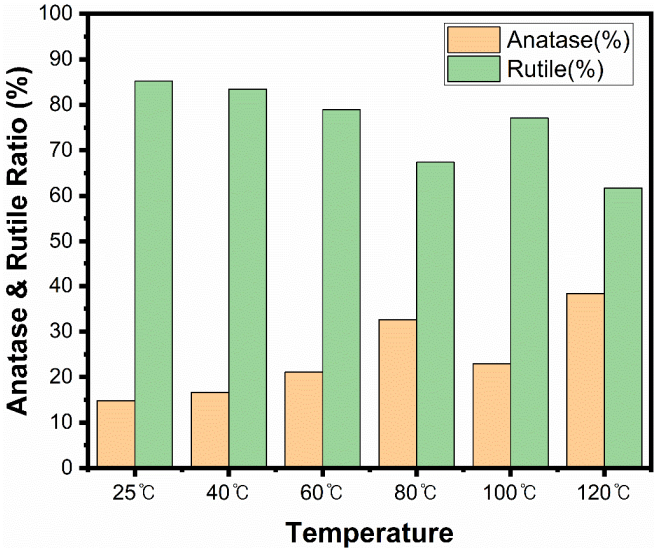

Fig. 3. Ratio of anatase to rutile under Condition I

0.080 mole. Since the particle size of TiO_2 precipitated from TiN process scrap is nano-size, it was analyzed using the Scherrer equation, Eq. (4). The particle size was increased with the amount of scrap. The TiO_2 particle size of condition II grew up to 5.7 nm, was an average size of 5 nm. It was thought that the particle size of precipitated TiO_2 were increased by the amount of Ti contained in the scrap.

The crystal structure of TiO_2 in Condition II showed a rutile crystal structure at mole ratios from 0.025 to 0.065. However, the mixed TiO_2 of anatase and rutile crystals were precipitated at 0.08 mole. This occurrence of anatase is thought to be due to the decrease in particle size according to Ibrahim and Sreekantan [19], TiO_2 produced via hydrothermal reaction from titanium isopropoxide and isopropyl alcohol using a sol-gel method forms anatase at low pH levels, and particle size decreased as pH decreases. However, in this study, it was confirmed that TiO_2 from scrap generated in the TiN film process exhibits a rutile

crystal structure even at very low pH 0 or less. But the mixed TiO_2 of rutile and anatase structures was formed at 0.08 mole, it was thought that increase of scrap's input leads to the mixed crystal structures of TiO_2.

The TiO_{22} by hydrothermal reaction of the scrap according to Condition I and Condition II had a particle size less than 10 nm. TiO_2 particles could be manufactured in the mixed crystal structures of Anatase and Rutile and the Rutile crystal structures depending on the reaction conditions. And This TiO_2 was heat treated to control the size and crystal structure in a tube furnace.

The heat treatment temperatures were set at 200, 400, 600, 800, and 1000°C, with lasting times of 0.5 hours and 1 hour, respectively. The heating rate was increased by 3°C/min, and cooling was carried out in air.

The TiO_2 particles of the Rutile crystal structure have improved crystallinity regardless of the heat treatment temperature and time. The changes in grain size according to variations in heat treatment temperature and duration were shown in Fig. 4, TiO_2 particle size was increased 4-6 nm to 123-145 nm.

The mixed TiO_2 of anatase and rutile was heat-treated according to temperatures and times respectively. The mixed TiO_2 of the anatase and rutile was transformed to Rutile when it was heated to 800°C or higher, regardless of the heat treatment time. This transformation occurs because the transition from anatase to Rutile starts around 650°C. And the crystallinity increased with increasing heat treatment temperatures [20-22].

The Figs. 4a) and 4b) are shown particle size change of TiO_2 of condition I and condition II after heat treatment respectively. The heated TiO_2 were increased from 4-6 nm to 140 nm, showed a larger growth rate after 800°C than the growth rate up to 600°C. The mixed TiO_2 of anatase and rutile, in Condition I, was changed to Rutile above 800°C, the growth rate of the particle size significantly increased with heat treatment temperature and times [23].

4. Conclusions

Nano-sized TiO_2 was produced by the hydrothermal reaction of scrap obtained from the TiN process trap on the reaction temperature and concentration. And heat treatment was subsequently performed to control the crystal structure and particle size of the TiO_2.The conclusions obtained in this study are as follows.

A solution produced by hydrothermal reaction using the scrap of TiN process was a strong acidic solution with a pH of 0 or less. Nanoparticle TiO_2 of 10 nm or less could be produced by controlling the reaction temperature and concentration.

The produced TiO_2 had a mixed TiO_2 structure of rutile and anatase depending on the reaction temperature, but the mixed TiO_2 appeared only at 0.08 mol under conditions depending on the reaction concentration.

When the reaction temperature was adjusted, the mixed TiO_2 had anatase and rutile crystal structure. At this time, the ratio of anatase ranged 14% to 38%. The particle size of TiO_2 generated by the hydrothermal reaction was about 4-8 nm and grew up to 140 nm by heat treatment. The mixed TiO_2 of anatase and rutile transformed into a rutile crystal structure at temperatures of 800°C or higher.

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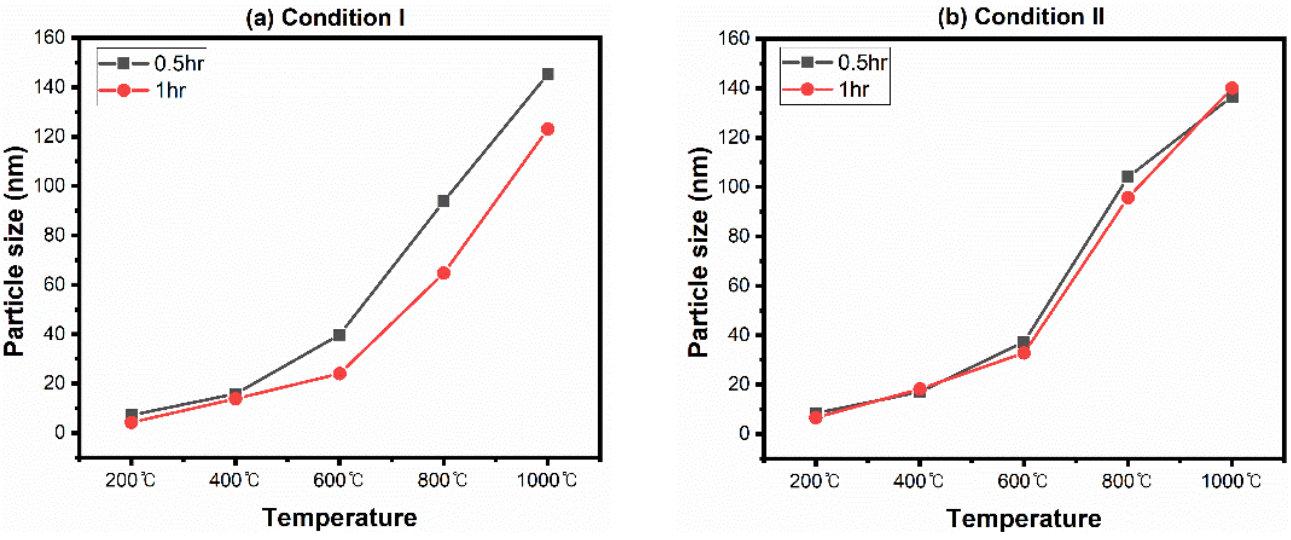

Fig. 4. Comparison of particle size in heat-treated samples under (a) Condition I and (b) Condition II

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