Synthesis of Au nanoparticle-incorporated mesoporous TiO₂ composite thin films and their electrical properties

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Mesoporous TiO₂ thin films containing Au nanoparticles were synthesized via sol-gel and evaporation-induced self-assembly processes. In this work, the effect of surfactant concentration on the pore structure of mesoporous TiO₂ thin films was investigated and Au nanoparticles were introduced to enhance the electrical conductivity of mesoporous TiO₂ without collapse of the pore structure. Pore structure was analyzed with small angle X-ray diffraction (SAXRD) and grazing incidence small angle X-ray scattering (GISAXS) was also used to investigate the pore arrangement at the 3C beam line (λ = 1.54 Å) to investigate pore structure ordering from 0.5 to 5° 2 theta (°). Grazing incidence small angle X-ray scattering (GISAXS) was also used to investigate the pore arrangement at the 3C beam line (λ = 1.54 Å and ∆λ/λ = 5 × 10⁻⁴) of the Pohang Light Source (PLS) in the Republic of Korea. Porosity was calculated using an ellipsometer (Gatan 4111, 632.8-nm He–Ne laser) and the Lorentz-Lorenz equation. Electrical conductivity was obtained using Hall Effect measurement (Ecopia HMS3000).

1. Introduction

Since ordered mesoporous silica was reported for the first time in 1992, interest in mesoporous structures has markedly increased due to their unique properties, such as low density, low thermal conductivity, and high specific surface area. Mesoporous materials have pore sizes ranging from 2 to 50 nm. Among many mesoporous oxides, mesoporous TiO₂ is popular because it can be used in many applications, including as a photocatalyst or gas sensor. Mesoporous TiO₂ can be synthesized by evaporation-induced self-assembly (EISA) processes when the surfactant concentration exceeds the critical micelle concentration (CMC). These micelles form a mesoporous structure after calcination. A mesoporous structure is applied to thermoelectric materials because of its low thermal conductivity, depending on porosity. Among many materials, TiO₂ has been primarily researched because of a proper Seebeck coefficient property. However, mesoporous TiO₂ has limitations due to its low figure of merit (ZT), which results from low electrical conductivity. The figure of merit can be expressed as ZT=S²/κT, where S, κ, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature, respectively. To increase the ZT value of a mesoporous structure, an increase in electrical conductivity without a corresponding collapse of pore structure is very important, because irregularities in an ordered mesoporous structure induce electron scattering. In this work, Au nanoparticles were incorporated into ordered mesoporous TiO₂ thin films to increase electrical conductivity, while maintaining the phonon-glass electron-crystal effect. The effects of surfactant concentration and incorporation of Au nanoparticles on the pore arrangement of mesoporous TiO₂ thin films were investigated and crystallization, pore structure, porosity, and electrical properties of the films were analyzed.

2. Experimental procedures

Sol-gel and EISA processes were used to synthesize mesoporous TiO₂ thin films containing Au nanoparticles. Titanium tetraisopropoxide [Ti(OR)₄], TTIP, Sigma Aldrich, 97%), n-propanol and Pluronic P-123 (EO₂₀PO₇₀EO₂₀, MW 5800, Sigma Aldrich) were used as TiO₂ precursor, solvent and surfactant, respectively. HCl (Duksan, 35 %) was used as an acidic catalyst to control the reaction rate of the sol-gel process. A varied surfactant to TiO₂ precursor (TTIP) molar ratio was used: 0, 0.005, and 0.015. The molar ratio of TTIP:P-123:HCl:n-propanol was 1:(0, 0.005, 0.015):8.42:13.2. In this experiment, 0.8037 g of purchased Au nanoparticle solution (Sigma Aldrich, 5 nm diameter, 0.1 mM concentration, 5.5 × 10⁻³ mL numbers) was added to 3 g of TTIP. This amount corresponds to 0.25 vol % of Au nanoparticle solution to TTIP or 0.035 vol % of Au nanoparticle to TTIP.

Solutions were spin-coated onto SiO₂/Si substrate after aging for 15 min. As-prepared films were aged at 80°C for 5 days to control the condensation reaction rate. After aging, the films were annealed at 450°C for 8 h under vacuum and to form mesoporous structure. Small angle X-ray diffraction (SAXRD) was performed with CuKα radiation (λ = 1.5418 Å) to investigate pore structure ordering from 0.5 to 5° 2 theta (°). Grazing incidence small angle X-ray scattering (GISAXS) was also used to investigate the pore arrangement at the 3C beam line (λ = 1.54 Å and ∆λ/λ = 5 × 10⁻⁴) of the Pohang Light Source (PLS) in the Republic of Korea. Porosity was calculated using an ellipsometer (Gatan L117C, 632.8-nm He–Ne laser) and the Lorentz-Lorenz equation. Electrical conductivity was obtained using Hall Effect measurement (Ecopia HMS3000).

3. Results and discussion

Crystallization of mesoporous TiO₂ thin films with or without Au nanoparticles was analyzed using wide angle X-ray diffraction. Crystallization of TiO₂ was analyzed with wide angle X-ray diffraction. Increased surfactant concentration led to a corresponding increase in the porosity of mesoporous TiO₂ thin films, but pore ordering in the mesoporous structure was still enhanced. The increasing rate of electrical resistivity associated with increased porosity was reduced in response to decreases in the electron scattering probability, which are strongly dependent on the pore ordering of mesoporous structures. Furthermore, the electrical conductivity of mesoporous TiO₂ composite thin films was enhanced by the incorporation of Au nanoparticles due to the surface plasmon effect of Au nanoparticles.

Key-words : Mesoporous TiO₂, Au nanoparticles, Electrical conductivity

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tion from 20 to 60°, and results are given in Figs. 1(a) and 1(b), respectively. Only results for the anatase phase were obtained for both TiO₂ films because low annealing temperature was progressed (450°C). Anatase phase is stable under 600°C. The presences of Au nanoparticles and Pluronic P-123 surfactant did not affect the phase formation of TiO₂ films with anatase structure; however, their presence did seem to affect the crystallinity of TiO₂ films. The diffraction peak intensity of Au nanoparticle-incorporated mesoporous TiO₂ composite thin films [Fig. 1(b)] was relatively weaker than that of mesoporous TiO₂ thin films without Au nanoparticles [Fig. 1(a)]. When the tri-block copolymer P-123 surfactant with dual hydrophobic and hydrophilic properties formed the micelle structure, Au nanoparticles stuck to the hydrophilic portion of the surfactant. After annealing, remaining Au nanoparticles mainly appeared outside of the micelle structure, i.e., in the TiO₂ skeleton structure. Thus, Au nanoparticles could act as a grain growth inhibitor in TiO₂ skeleton structures. However, the diffraction peak of Au nanoparticles was not observed due to their small size (5 nm) and the small amount present (1.36 vol % of TiO₂ precursor). For both samples, incorporation of the surfactant might induce a slight degradation in crystallinity. As shown in the figure, TiO₂ thin films without surfactant (TiO₂₀ or Au-TiO₂₀) exhibited a relatively strong diffraction peak compared with other mesoporous TiO₂ thin films (TiO₂₀.005, TiO₂₀.015 or Au-TiO₂₀.005, Au-TiO₂₀.015). Here, 0.005 and 0.015 represent the surfactant to TiO₂ precursor molar ratio. When the surfactant molar ratio increased, the diffraction peak intensity decreased slightly because the micelle structure could inhibit grain growth in the TiO₂ skeleton structure.

SAXRD was investigated from 0.5 to 5° 2θ to analyze pore structure according to Au nanoparticle incorporation and various surfactant concentrations. SAXRD results of mesoporous TiO₂ thin films with or without Au nanoparticles are shown in Figs. 2(a) and 2(b), respectively. In the case of dense-TiO₂ thin films (TiO₂₀ or Au-TiO₂₀), an SAXRD peak was not observed because an ordered pore structure could not be synthesized without surfactant. However, with a surfactant concentration of 0.005, a diffraction peak was clearly observed at 0.8° 2θ and the intensity increased at a surfactant concentration of 0.015 mol % because of enhanced pore arrangement. As the surfactant molar ratio increased, the SAXRD peak shifted to a higher angle because the number of micelles increased with increased surfactant concentration and wall thickness consequently decreased. The incorporation of Au nanoparticles did not affect the pore ordering in the ordered mesoporous TiO₂ films, as indicated by the similar SAXRD peak intensities of both samples. As discussed earlier, most nanoparticles were distributed in the TiO₂ skeleton structure and there were almost no effect on micelle formation. From the SAXRD results, inter-pore distance (d-spacing) was calculated to be 10.9 and 9.8 nm for 0.005 and 0.015 surfactant concentrations, respectively, regardless of Au nanoparticle incorporation. GISAXS analysis of the mesoporous TiO₂ composite thin films was carried out to analyze the pore structure.
according to surfactant concentration and Au nanoparticle incorporation in greater detail. GISAXS includes the information of arranged structure in film such as particle, block copolymer, pore, and so on. According to the direction of arrangement (parallel or vertical from substrate), peak position is changed. And with an increase of arrangement, peak intensity is increased. As shown at Figs. 3(a) and 3(b), this soaring both side patterns is called “wing pattern”. As shown in Figs. 3(a) and 3(b), pore arrangement could be identified by using GISAXS. Inter-pore distance of ordered mesoporous structure and alignment direction of pore could be analyzed using the position and intensity of GISAXS wing pattern. A horizontal arrangement of mesoporous structure could be confirmed with Figs. 3(a) and 3(b). When pore ordering increases, pores are arranged with an equal interval and GISAXS peak intensity is increased. In this work, wing pattern intensity was increased with increasing surfactant concentration because the number of micelle was increased and ordered pore structure was well developed. However, GISAXS wing pattern intensity of Au nanoparticle incorporated mesoporous TiO2 thin film does not show an important difference from the mesoporous TiO2 thin film. From this GISAXS result and SAXRD result given in Fig. 2, it can be said that the presence of Au nanoparticle did not affect much on the arrangement of pores in mesoporous TiO2 films. Porosity measured via an ellipsometer was used to analyze the effect of surfactant concentration and Au nanoparticle incorporation, and the results are presented in Fig. 4. Porosities of mesoporous TiO2 thin films with or without Au nanoparticles were calculated using the Lorentz-Lorenz equation. 

\[
1 - F_p = \frac{n_f^2 - 1}{n_f^2 + 2} = \frac{n_s^2 - 1}{n_s^2 + 2}
\]

(1)

Where \( F_p \) is the pore volume fraction, \( n_f \) is the refractive index of film, and \( n_s \) is the refractive index of base structure in air. To calculate the porosity by using Lorentz-Lorenz equation, the refractive index of pure TiO2 (anatase phase) and Au nanoparticle incorporated mesoporous TiO2 are required. In this work, refractive indices of TiO2 with anatase phase and Au nanoparticle incorporated mesoporous TiO2 were fixed as 2.500 and 2.469, respectively \( [n_s \text{ value in Eq. (1)}] \). And, refractive index of composite thin film \( [n_f \text{ value in Eq. (1)}] \) was obtained by using ellipsometer and presented in Table 1. In the case of Au nanoparticle incorporated mesoporous TiO2 composite thin films, porosity values were a little smaller than those of mesoporous TiO2 thin films because of slight inhibition behavior of incorporated Au nanoparticles on the formation of mesoporous structure. This slight disturbance behavior was already confirmed.

![GISAXS patterns](image1)

Fig. 3. GISAXS patterns of (a) mesoporous TiO2 thin films and (b) Au nanoparticle-incorporated mesoporous TiO2 composite thin films with various surfactant concentrations.

![Porosity graph](image2)

Fig. 4. Porosity of mesoporous TiO2 thin films and Au nanoparticles-incorporated mesoporous TiO2 composite thin films with various surfactant concentrations.

| Surfactant ratio (mol %) | Mesoporous TiO2 | Mesoporous Au-TiO2 |
|-------------------------|-----------------|-------------------|
| 0                       | 2.240           | 2.229             |
| 0.005                   | 2.075           | 2.143             |
| 0.015                   | 1.809           | 1.877             |

Table 1. Refractive index of mesoporous TiO2 and Au nanoparticles incorporated mesoporous TiO2 composite
in the SAXRD and GISAXS results. In 0.015 mol % surfactant concentration samples, porosity decreased from 32.3 to 27.4% after Au nanoparticle incorporation. The porosity data infers that Au nanoparticles interfere with the formation of pore structure and induce slight decreases in film porosity.14)

Electrical resistivity values of mesoporous TiO_2 thin films with or without Au nanoparticles are given in Fig. 5. When comparing with the resistivity of non-porous TiO_2 (without surfactant) and that of mesoporous TiO_2-0.005, the resistivity was increased with surfactant concentration. This increment was followed by the presence of pore which behaves as a scattering center on the electrical conductivity. As a result, the resistivity was increased about 5 times although only 7% of porosity was introduced in the non-porous TiO_2. For the mesoporous TiO_2 films, the porosity was increased linearly with increasing surfactant concentration but with regular distribution of pores. The resistivity increase was relatively small when comparing with an increase of porosity because an electron scattering effect could be minimized with regular distribution of pores. The several nanometer scale of inelastic mean free path (IMFP) of electron might reduce the effect of increasing porosity in mesoporous TiO_2 films on the electrical conductivity.15) Au nanoparticle was incorporated to increase an electrical conductivity from the surface plasmon effect of Au nanoparticle because surface plasmon effect could affect on the electrical conductivity. When Au nanoparticles are incorporated in base material, energy band structure is changed to downward band bending.16) So, as shown in Fig. 5, mesoporous Au-TiO_2 composite films have relatively lower resistivity than mesoporous TiO_2 films. This surface plasmon effect was identified from the comparison of the resistivity values of mesoporous TiO_2-0.005 and Au-TiO_2-0.015 films. These two samples has similar resistivity value but Au-TiO_2-0.015 film has 7% higher porosity value than that of mesoporous TiO_2-0.005. Au nanoparticle-incorporated mesoporous TiO_2 thin films could exhibit enhanced thermoelectric properties due to the relatively small decrease in their electrical resistivity induced by a large increase in porosity, which generally has an inverse relationship with thermal conductivity.

4. Conclusions

Mesoporous TiO_2 thin films with or without Au nanoparticles were synthesized via sol–gel and EISA processes. Incorporation of Pluronic P-123 surfactant and Au nanoparticles affected grain growth of the anatase-phase TiO_2 skeleton structure. Pore ordering in mesoporous structures was enhanced when surfactant concentration increased from 0.005 to 0.015. This enhancement of pore arrangement induced a decrease in electron scattering probability; relatively small increases in electrical resistivity were observed even with large increases in porosity. When Au nanoparticles were incorporated, there was no noticeable influence on ordered pore structure in this experimental condition. The surface plasmon effect of Au nanoparticles incorporated into ordered mesoporous TiO_2 structures decreased the increase in electrical resistivity associated with porosity.

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