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Research Article

Effect of Surfactant Concentration Variation on the Thermoelectric Properties of Mesoporous ZnO

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The electrical and thermal conductivities and the Seebeck coefficient of mesoporous ZnO thin films were investigated to determine the change of their thermoelectric properties by controlling surfactant concentration in the mesoporous ZnO films, because the thermoelectric properties of mesoporous ZnO films can be influenced by the porosity of the mesoporous structures, which is primarily determined by surfactant concentration in the films. Mesoporous ZnO thin films were successfully synthesized by using sol-gel and evaporation-induced self-assembly processes. Zinc acetate dihydrate and Brij-76 were used as the starting material and pore structure-forming template, respectively. The porosity of mesoporous ZnO thin films increased from 29% to 40% with increasing surfactant molar ratio. Porosity can be easily altered by controlling the molar ratio of surfactant/precursor. The electrical and thermal conductivity and Seebeck coefficients showed a close correlation with the porosity of the films, indicating that the thermoelectric properties of thin films can be changed by altering their porosity. Mesoporous ZnO thin films with the highest porosity had the best thermoelectric properties (the lowest thermal conductivity and the highest Seebeck coefficient) of the films examined.

1. Introduction

The acceleration in global warming has made development of alternative energy sources of critical importance to modern society. Among many alternative energy technologies, thermoelectric technology refers to creation of an electrical current in a material with a temperature gradient. High electrical conductivity, a high Seebeck coefficient, and low thermal conductivity are essential characteristics of thermoelectric materials. Although it is very difficult to control these factors individually, because electrical conductivity and the Seebeck coefficient have an inverse relationship, this problem can be overcome by the use of nanostructures, such as nanowires and superlattices [1].

Mesoporous structures are those with a pore diameter ranging from 2 to 50 nm [2]. Compared with nonporous structures, mesoporous structures have excellent physical and

chemical properties. Because of their pore structure, mesoporous materials have unique properties such as low thermal conductivity and high specific surface area. They can potentially be used in gas sensor applications and in thermoelectric devices, among many other applications. However, these materials should have a high Seebeck coefficient and electrical conductivity and low thermal conductivity when applied in thermoelectric devices. Although mesoporous structures have low thermal conductivity property, this is accompanied by a decrease in electrical conductivity. By controlling porosity and pore size, this limitation can be overcome. Electrical conductivity and thermal conductivity have different inelastic mean free paths from each other. The inelastic mean free path of an electron is four times longer than that of a phonon. This difference can induce the phonon-glass electron-crystal (PGEC) effect. By exploiting this effect in mesoporous structures, electrical conductivity and thermal

conductivity can be controlled separately. Furthermore, the thermoelectric properties of a material can be improved by adopting a mesoporous structure.

Zinc oxide (ZnO) is an inexpensive, n-type, wide band gap semiconductor material that has excellent electronic, optic, and photonic properties. It is, therefore, used in photovoltaic [3], gas sensor [4], and laser [5] applications, among many others. ZnO thin films can be synthesized by various techniques such as spray pyrolysis, RF sputtering, chemical vapor deposition (CVD) and sol-gel processes [6–8]. Among these methods, we adopted the sol-gel method in this study because this is a low-cost procedure and it offers easy control of film thickness and composition. However, the low crystallization temperature of ZnO and high reactivity of Zn ion precursors makes it difficult to create mesoporous ZnO [9–11]. During annealing for calcination, the pore structure can easily collapse because of crystallization of ZnO with a hexagonal wurtzite structure at low temperature. Furthermore, it is more difficult to obtain a three-dimensional network structure of ZnO because it is harder to form Zn–O bonds than Si–O or Ti–O bonds during hydrolysis because of the high reactivity of the Zn ion precursor. Low temperature annealing and stable conditions are required to address these problems. By using a block copolymer with a low molecular weight and a complex agent, mesoporous ZnO thin films can be synthesized successfully. In this paper, we investigated the effect of the molar ratio of surfactant/precursor on the formation of mesoporous ZnO thin films and the crystallization, pore structure, porosity, and thermoelectric properties of the resultant films.

2. Experimental Procedure

Mesoporous ZnO thin films were synthesized on SiO₂/Si substrates by sol-gel and spin coating processes. In this work, n-propanol, zinc acetate dihydrate [Zn(CH₃COO)₂·H₂O], and monoethanolamine (MEA) were used as the solvent, precursor and complex agent, respectively. Brij-76 (C₅₈H₁₁₈O₂₁, Aldrich, MW 711), which forms micelle structures, was used as a surfactant. MEA acts as a stabilizer in ZnO sol as well as a pH-increasing agent. Addition of MEA to ZnO sol causes the ZnO matrix to adopt a rigid structure. In this work, the molar ratio of MEA/Zn precursor was fixed at 1 to allow us to investigate the effect of the molar ratio of surfactant/precursor on the pore structure of mesoporous ZnO.

The molar ratio of zinc acetate dihydrate : Brij-76 : MEA : n-propanol was 1 : 0.03~0.09 : 1 : 34.5. surfactant/precursor molar ratios were 0.03, 0.05, and 0.09, which we indexed as Z3*/Z3, Z5*/Z5, and Z9*/Z9 before/after the annealing process, respectively. Mesoporous ZnO thin films were prepared by spin coating this solution onto SiO₂/Si substrate through the evaporation-induced self-assembly (EISA) process [12, 13]. After coating, thin films were preheated at 300°C for 10 min to pyrolysis the ZnO precursor and remove residual organics. Mesoporous ZnO thin films were synthesized after annealing at 450°C for 4 h under vacuum. To analyze the mesoporous structures, small angle X-ray diffraction (SAXRD) was performed with angles ranging from 1° to 5° using CuKα radiation (1.5418 Å).

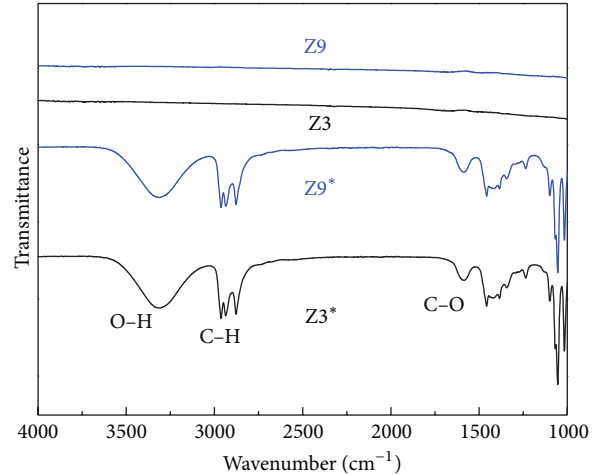


FIGURE 1: FT-IR spectra of mesoporous ZnO thin films produced using various surfactant concentrations before annealing (Z3*, Z9*) and after annealing (Z3, Z9) at 450°C.

The pore structure and ordering was analyzed by transmission electron microscope (TEM, JEOL JEM-2100F) at 400 kV. The porosity of mesoporous ZnO thin films was measured using an ellipsometer (Gatan L117C, 632.8 nm He-Ne lasers) and the Lorentz-Lorenz equation [14]. For thermal conductivity measurements of mesoporous ZnO film, the 3 ω method measurement was performed at 300 K [15]. The Seebeck coefficients and the electrical resistivity of mesoporous ZnO films were measured by detecting the Seebeck voltage and the temperature difference from 323 K to 478 K with an interval of 50 K. Hall measurement equipment was used to measure the carrier concentration of mesoporous ZnO thin films.

3. Results and Discussion

Figure 1 shows the FT-IR spectra of mesoporous ZnO thin films before and after annealing at 450°C under vacuum. Low temperature annealing was performed to prevent the collapse of the pores. Before annealing, organic bonds were observed in ZnO samples, for example, Z3* and Z9* had broad peaks at approximately 3300 cm⁻¹, 2800 cm⁻¹, and from 1400 cm⁻¹ to 1700 cm⁻¹, corresponding to O–H, C–H, and C–O absorption peaks, respectively. We attributed these organic bond peaks to the surfactant (Brij-76) and complex agent (MEA). However, after annealing at 450°C under vacuum, the organic bonds disappeared completely for both the Z3 and Z9 samples, as shown Figure 1. These results indicate that the surfactant was completely removed by annealing at the low temperature of 450°C.

Figure 2 shows the SAXRD patterns of mesoporous ZnO thin films after annealing at 450°C. The existence of diffraction peaks indicates a regular pore distribution in the thin films. Broad diffraction peaks were observed around 2.17, 2.21, and 2.23° of 2 θ for Z3, Z5, and Z9 samples, respectively; this broadness means that the mesoporous ZnO thin films did not have high pore regularity but formed a partially ordered

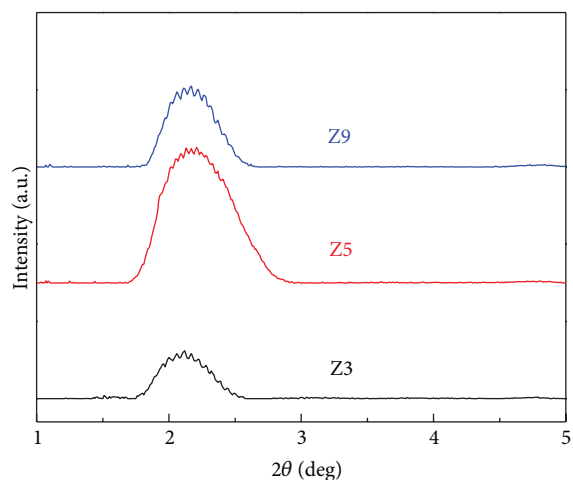


FIGURE 2: Small angle XRD patterns of mesoporous ZnO thin films synthesized using various surfactant concentrations.

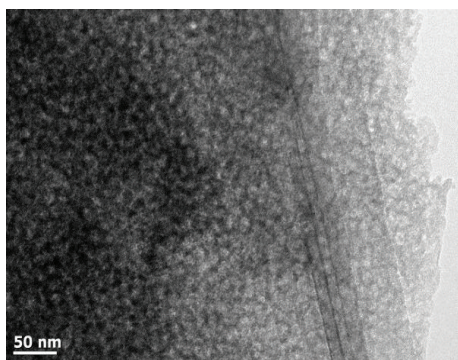


FIGURE 3: TEM image of a mesoporous ZnO thin film (Z5).

structure. From the diffraction 2θ data, the interplanar distances were calculated as 4.07, 3.99, and 3.96 nm for the Z3, Z5, and Z9 samples, respectively. These results indicate that as the surfactant molar ratio increased, so did the number of micelles per unit volume, while the thickness of the ZnO wall decreased [10]. The strongest diffraction intensity was observed for the Z5 sample; this means that the highest ordering of pores in mesoporous ZnO film was obtained at an optimized surfactant concentration. When the surfactant concentration was too low (Z3), a well-ordered micelle structure did not form because of negligible steric effects. When the surfactant concentration was too high (Z9), the regularly arranged micelle structure collapsed during calcination due to the decrease in mechanical strength with an increase in porosity. The partially ordered pore structure of Z5 could be confirmed from the TEM image, as seen in Figure 3. The image showed partially arranged, regularly spaced nanopores 8–9 nm in size, which was almost two times larger than the interplanar spacing obtained from the SAXRD data given in Figure 2. From the (200) indexation of the diffraction peak in SAXRD data and TEM data, mesoporous ZnO thin film could be suggested to have a partially ordered, body-centered cubic arrangement of pores.

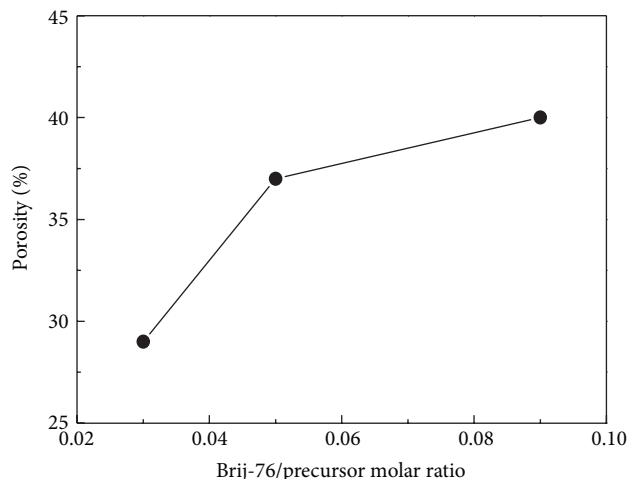


FIGURE 4: Porosity of mesoporous ZnO thin films synthesized using various surfactant concentrations.

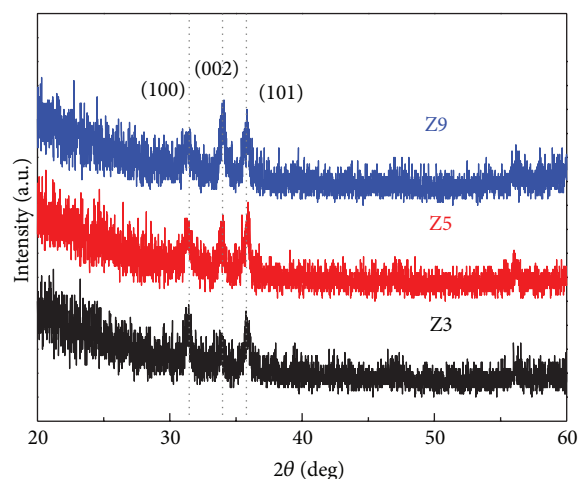


FIGURE 5: Wide-angle XRD patterns of mesoporous ZnO thin films synthesized using various surfactant concentrations.

Figure 4 shows the porosity behavior of mesoporous ZnO thin films. The porosity of the Z3, Z5, and Z9 films was measured as 29, 37, and 40%, respectively, and porosity increased with increasing surfactant molar ratio. However, in the case of the Z9 sample, the increase in porosity was small when considering the increase in the surfactant molar ratio; this was due to the collapse of pores, as shown in Figure 2.

Wide-angle XRD patterns of mesoporous ZnO thin films are shown in Figure 5. Mesoporous ZnO thin films were crystallized with a hexagonal wurtzite structure; the diffraction peaks at a 2θ of approximately 31.8° , 33.4° , and 36.2° were indexed as 100, 002, and 101, respectively. Comparison of diffraction intensity revealed that the surfactant concentration did not affect the crystallization of skeleton-structured ZnO.

Figure 6 shows the Seebeck coefficient of mesoporous ZnO thin films after annealing at 450°C at various surfactant/precursor molar ratios. Because ZnO is an n-type

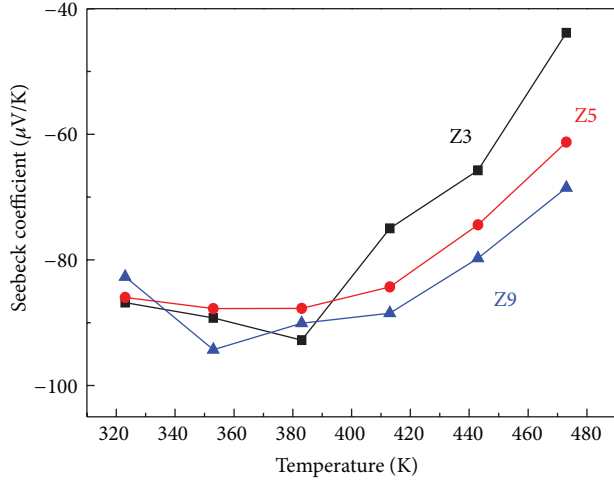


FIGURE 6: The Seebeck coefficient of mesoporous ZnO thin films synthesized using various surfactant concentrations.

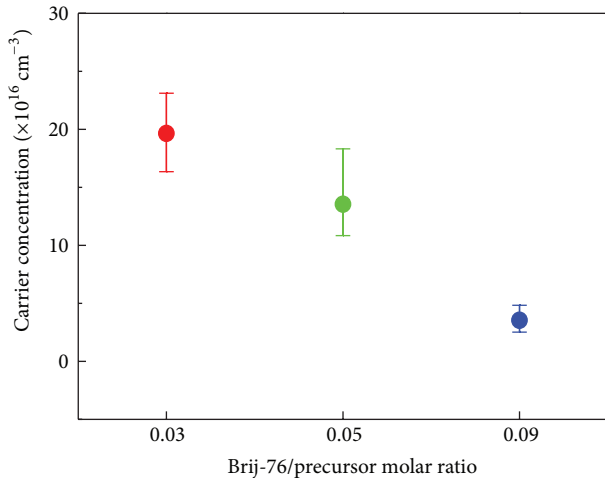


FIGURE 7: The carrier concentration of mesoporous ZnO thin films synthesized using various surfactant concentrations.

material, its Seebeck coefficient has a negative value. The Seebeck coefficient was affected by the surfactant/precursor molar ratio; when surfactant/precursor molar ratio increased, porosity also rose, inducing an increase of internal surface area which might act as a carrier trap site. The relationship between the carrier concentration and surfactant concentration was given in Figure 7. As shown in the figure, decreases in carrier concentration were observed with increasing surfactant concentration, that is, increasing porosity of the film. Thus, Seebeck coefficient was also increased due to its inverse relationship with carrier concentration. The Z9 sample, which had the highest porosity of 40% among the samples evaluated, had the highest the Seebeck coefficient at 353 K: $-94.3 \mu\text{V/K}$.

Figure 8 shows the electrical conductivity of mesoporous ZnO thin films according to surfactant concentrations. Generally, the Seebeck coefficient has an inverse relation with electrical conductivity. As porosity increases, electrons scatter

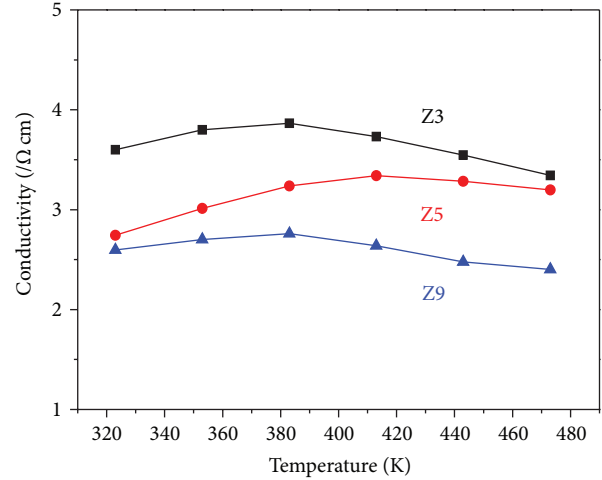


FIGURE 8: Electrical conductivity changes in mesoporous ZnO thin films synthesized using various surfactant concentrations.

and electrical conductivity decreases. Because the Z3 sample had the lowest porosity, its electrical conductivity was higher than those of the Z5 and Z9 samples. The average electrical conductivities values were 3.647 , 3.136 , and $2.596/\Omega\text{Cm}$ for the Z3, Z5, and Z9 samples, respectively. Although electrical conductivity decreased with increasing surfactant concentration, the decrease in electrical conductivity was small. Furthermore, in a mesoporous structure, if the Seebeck coefficient increases and thermal conductivity decreases, then the thermoelectric properties of the structure should improve.

Thermal conductivity values of mesoporous ZnO thin films are shown in Figure 9. As the surfactant/precursor molar ratio increased, thermal conductivity decreased due to the increase in porosity. The Z9 sample had the lowest thermal conductivity of 1.01 W/mK . These results, together with the increased porosity of mesoporous ZnO film, indicate that electrical conductivity and thermal conductivity decreased concomitantly. However, thermal conductivity decreased to greater extent than electrical conductivity.

Figure 10 shows the ratio of electrical conductivity to thermal conductivity according to various surfactant concentrations because the thermoelectric figure of merit shows a direct relationship with the electrical/thermal conductivity ratio. To calculate the conductivity ratio, the electrical conductivity value was used as an average term according to temperature. As the surfactant concentration increased, the conductivity ratio also increased from 180.54 K/V^2 to 257.03 K/V^2 . This increase can be explained by the PGEC effect. With increasing porosity, the number of pores also increases, and phonons can be scattered effectively because of the pores. During this process, phonon scattering is higher than electron scattering because the phonon inelastic mean free path is generally known to be shorter than that of electrons [16]. Our conductivity ratio results indicate that the thermoelectric properties of mesoporous ZnO thin films can be enhanced by controlling their porosity. The Z9 sample had the highest conductivity ratio and the largest negative Seebeck coefficient. Therefore, by controlling the porosity of

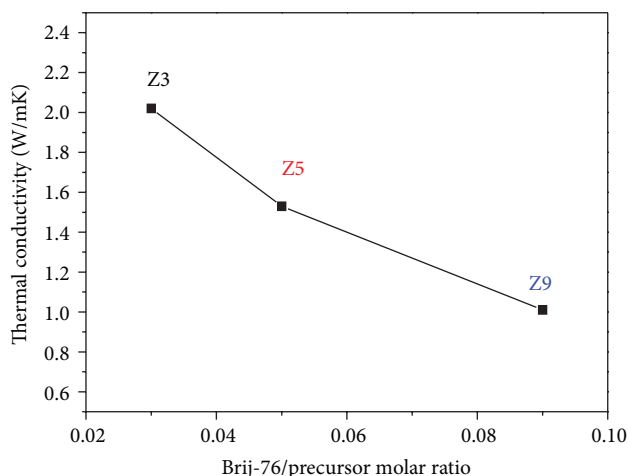


FIGURE 9: Thermal conductivity of mesoporous ZnO thin films synthesized using various surfactant concentrations.

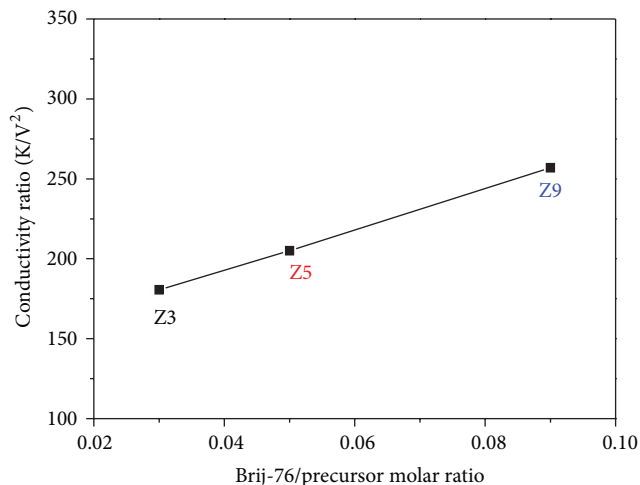


FIGURE 10: Conductivity ratio of mesoporous ZnO thin films synthesized using various surfactant concentrations.

mesoporous structures, their thermoelectric properties can be improved.

4. Conclusions

We synthesized mesoporous ZnO thin film using sol-gel and EISA processes with zinc acetate dihydrate, MEA, and Brij-76. Porosity of mesoporous ZnO thin films was varied from 29% to 40% by adjusting the precursor/surfactant molar ratio from 0.03 to 0.09. As the porosity of the thin films increased, the Seebeck coefficient was increased due to a decrease in carrier concentration. The maximum Seebeck coefficient at 353 K and the maximum electrical/thermal conductivity ratio were obtained at a surfactant/precursor molar ratio of 0.09. By increasing the porosity of the ZnO thin films, their conductivity ratio and Seebeck coefficients increased. In other words, the higher the porosity of mesoporous ZnO thin films, the better their thermoelectric properties.

Acknowledgments

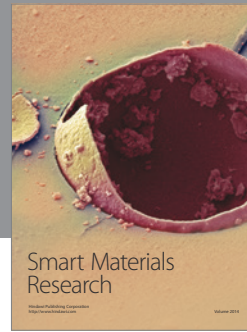
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