

Crystallization and Optical Properties of ZnO-MO_x Films (M=Al, Ti, Zr) Deposited by Sol-Gel Method

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The effects of MO_x (M=Al, Ti, Zr) addition on the microstructure, crystallization behavior and optical properties of ZnO-MO_x films deposited by sol-gel method were investigated. Zinc acetate dihydrate (Zn(OCOCH₃)₂ · 2H₂O), ethanolamine and 1-propanol were used as a starting material, stabilizer and solvent, respectively. Aluminum sec-butoxide, titanium i-propoxide and zirconium n-propoxide were used as MO_x sources. The surface morphology of ZnO-MO_x films fired at 500°C depended on the kind of MO_x. In ZnO-AlO_{1.5} film, the corrugated structure and cracks were observed. In contrast, the surface of ZnO-ZrO₂ film was flat with no crack. The grain size of the ZnO-ZrO₂ film was large (approximately 80 nm) compared with ZnO-AlO_{1.5} and ZnO-TiO₂ films. The higher crystallinity was obtained in ZnO-ZrO₂ ([Zn]/[Zr]=80/20) film compared with other ZnO-MO_x films. The addition of AlO_{1.5} or TiO₂ resulted in the suppression of grain growth and crystallization in the films. As a result, only ZnO-ZrO₂ ([Zn]/[Zr]=80/20) film exhibited higher transmittance (~90%) in the visible region and higher shielding property (>90%) in the ultraviolet ray region.

Key words: Sol-gel method, Zinc oxide-metal oxide, Optical property, Dip coating

1. INTRODUCTION

Zinc oxide (ZnO) has been widely used in various applications such as transparent conducting electrodes in display, semiconductors in optoelectronic devices, piezoelectric devices and ultraviolet ray (UV) shielding agent [1-3]. UV shielding coating for automotive windows and headlamp lens is required high transmittance in the visible region and high absorbance in the UV region. ZnO is a suitable material for this application because of its wide band gap of 3.3 eV.

ZnO films are prepared by various methods such as sputtering [4], chemical vapor deposition (CVD) [5], pulsed laser deposition (PLD) [6], spray pyrolysis [7] and sol-gel method [8]. The sol-gel method is more convenient and cost effective, and therefore it has been extensively used for preparing various oxide films. To prepare the ZnO film with high UV shielding property, relatively thick ZnO film is needed. Y. S. Kim et al. prepared the desired thickness of ZnO film through sol-gel method by repeating the spin coating five times during drying procedure [9], because it is usually difficult to obtain a relatively thick film by sol-gel method more than 100 nm thick for one coating operations. Furthermore, ZnO gel film derived from sol-gel precursor solution is low stability to moisture in air, resulting the translucent film.

In this work, the ZnO-MO_x (M=Al, Ti and Zr) films were deposited by sol-gel dip coating to

improve the above properties of ZnO film. The effects of MO_x addition on the stability of the precursor gel film and the microstructure of the resulting ZnO-MO_x films were investigated. In addition, the optical properties as well as crystallization behavior of the resulting films were also reported.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of ZnO-MO_x precursor solution and deposition of films

Fig. 1 shows the preparation method of ZnO - MO_x (M=Al, Ti and Zr) precursor solutions.

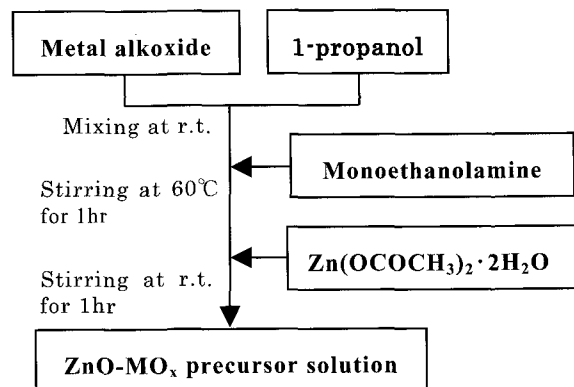


Fig. 1 Flow chart showing preparation procedure of ZnO-MO_x precursor solution

Zinc acetate dihydrate ($\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$) was used as Zn source. Aluminum sec-butoxide ($\text{Al}(\text{OC}_4\text{H}_9)_3$), titanium i-propoxide ($\text{Ti}(\text{OC}_3\text{H}_7)_4$) and zirconium n-propoxide ($\text{Zr}(\text{OC}_3\text{H}_7)_4$) were used as Al source, Ti source and Zr source, respectively. 1-propanol and monoethanolamine (hereafter MEA) were used as solvent and stabilizer. M-source was first dissolved in 1-propanol at room temperature. MEA was added to the M-source solution and stirred at 60°C for 1 hour. Zinc acetate was finally mixed with the resultant solution at room temperature for 1 hour. The molar ratio, $[\text{MEA}]/([\text{Zn}]+[\text{M}])$ was fixed at 0.72 and concentration of zinc acetate was 1 mol/l. the molar ratio, $[\text{Zn}]/[\text{M}]$ was varied between 100/0 to 80/20.

ZnO-MOx films were deposited on soda lime glass substrates by the dip-coating method. The withdrawal speed was fixed at 400mm/min. After deposition by the dip-coating, the samples were dried at 80°C for 3 hours and fired at 500°C for 30 min.

2.2 Characterization

The thermal decomposition behavior of the gels obtained by drying the solution at 80°C was examined by thermogravimetry-differential thermal analyzer (TG-DTA, Seiko Exster 6300).

Crystalline phases in the resultant films were identified by X-ray diffraction (XRD) using a $\text{CuK}\alpha$ radiation. Surface and cross-sectional morphology of the films were observed by a scanning electron microscope (FE-SEM, Hitachi S-4700). Optical transmittance measurements were carried out using an ultraviolet visible near-infrared spectrophotometer (Hitachi, U-4000).

3. RESULTS AND DISCUSSION

3.1 Thermal analysis of the dried ZnO-MOx gels

Fig. 2 shows TG-DTA curves of the dried ZnO-MOx gels. In all TG curve of ZnO-MOx gels, three weight losses were observed at $100\text{--}150^\circ\text{C}$, $200\text{--}250^\circ\text{C}$ and $300\text{--}400^\circ\text{C}$. The first weight loss is due to the evaporation of water. Second and third weight losses are caused by the combustion of residual organics such as acetate group, alkoxy groups and MEA. One large exothermic peak was found at $350\text{--}400^\circ\text{C}$ in DTA curves. The peak may be caused by the combustion of residual organics and by the crystallization of ZnO.

In ZnO- $\text{AlO}_{1.5}$ gels, the exothermic peak in DTA curves of 90/10 gel and 80/20 gel was found at 384°C and 394°C , respectively. The exothermic peak temperature increased with increase in Al content of the gel. The weight loss corresponding to the combustion of residual organics decreased with increase in Al content. Increase in Al content means increase of butoxy group from Al-butoxide as Al source, nevertheless residual organics in the gel decreased with Al addition. This indicates that butoxy group of Al-butoxide hydrolyze or react with MEA to form butanol, following to removal during drying. As a result, the weight loss caused

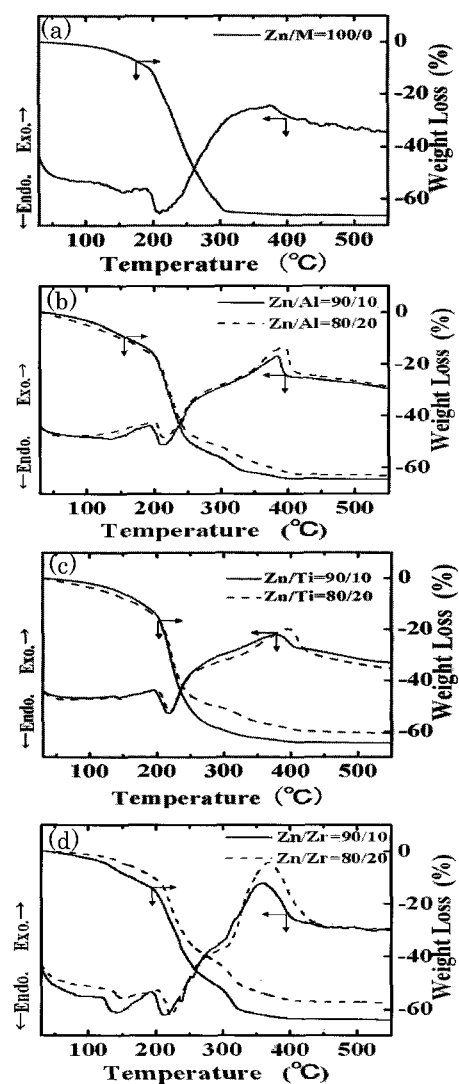


Fig. 2 TG-DTA curves of ZnO-MO_x gels dried at 80°C . (a) ZnO, (b) ZnO- $\text{AlO}_{1.5}$, (c) ZnO- TiO_2 , (d) ZnO- ZrO_2

by combustion of residual organics decreased with increase of Al content.

In ZnO- TiO_2 gels, the exothermic peak in DTA curves of 90/10 gel and 80/20 gel was found at 378°C and 396°C , respectively. The exothermic peak temperature increased with increase in Ti content of the gel same as the case of ZnO- $\text{AlO}_{1.5}$ gels. The weight loss corresponding to the combustion of residual organics decreased with increase in Ti content same as the case of ZnO- $\text{AlO}_{1.5}$ gels.

In ZnO- ZrO_2 gels, the exothermic peak in DTA curves of 90/10 gel and 80/20 gel was found at 359°C and 370°C , respectively. The temperatures of these peaks were low compared with ZnO- $\text{AlO}_{1.5}$ gels and ZnO- TiO_2 gels. The weight loss decreased with increase in Zr content same as the case of ZnO- $\text{AlO}_{1.5}$ gels and ZnO- TiO_2 gels.

3.2 Deposition and crystallization of ZnO-MO_x films

Table I shows the appearance of ZnO-MO_x dried films at 80°C and fired films at 500°C. ZnO-MO_x films were deposited on glass substrate by once dip coating operation.

Table I Appearance of ZnO-MO_x dried films and fired films

M	[Zn]/[M]	Dried Gel	Fired film
-	100/0	△	×
Al	90/10	⊙	×
	80/20	⊙	○
Ti	90/10	⊙	×
	80/20	⊙	○
Zr	90/10	⊙	×
	80/20	⊙	⊙

⊙:transparent and crack free, ○:transparent and crack, △:translucent and crack free, ×:translucent and crack

Every ZnO-MO_x precursor solution used to the deposition was clear. However, dried film of ZnO (100/0) was cloudy. The film changed clear to cloudy during the drying at 80°C in air. Other dried films [ZnO-MO_x (M=Al, Ti, Zr 90/10 and 80/20)] were transparent. These results indicated that deposited films from the precursor solutions containing M component were more stable to moisture in air than the pure ZnO gel film. This result suggested that the metal alkoxide reacted with zinc acetate and monoethanolamine, forming more stable precursor to water in 1-propanol solvent.

After firing at 500°C, ZnO (100/0) film, ZnO-AlO_{1.5} (90/10) film, ZnO-TiO₂ (90/10) film and ZnO-ZrO₂ (90/10) film were translucent but ZnO-AlO_{1.5} (80/20) film, ZnO-TiO₂ (80/20) film and ZnO-ZrO₂ (80/20) film were transparent. Only ZnO-ZrO₂ (80/20) film was crack free.

Fig. 3 shows XRD patterns of ZnO-MO_x films fired at 500°C. ZnO (100/0) film exhibited three main peaks corresponding to the (100), (002), and (101) planes of ZnO wurzite structure. In ZnO-AlO_{1.5} films, the intensities of XRD peaks corresponding to ZnO considerably decreased compared with ZnO (100/0). The XRD peaks corresponding to aluminum oxide were not confirmed in both films 90/10 and 80/20.

The intensity of ZnO(002) peak of ZnO-TiO₂ (90/10) film was high compared with ZnO(100) peak and (101) peak, but the intensity of three peaks decreased compared with ZnO (100/0) film. The three peaks of ZnO-TiO₂ (80/20) film were further small. These results indicated that the suppression of crystallization occurred by increasing the Ti content in the film. These results also agreed with the result that increased the exothermic peak temperature with increase of Ti content in TG-DTA. The XRD peaks corresponding to titanium oxide were not confirmed in both films 90/10 and 80/20.

In case of ZnO-ZrO₂ films, the intensities of XRD peaks corresponding to ZnO decreased compared with ZnO (100/0) film but increased compared with other ZnO-AlO_{1.5} and ZnO-TiO₂ films. Tetragonal ZrO₂ (101) peak appeared in ZnO-ZrO₂ (80/20) film added to ZnO (100), (002) and (101) peaks.

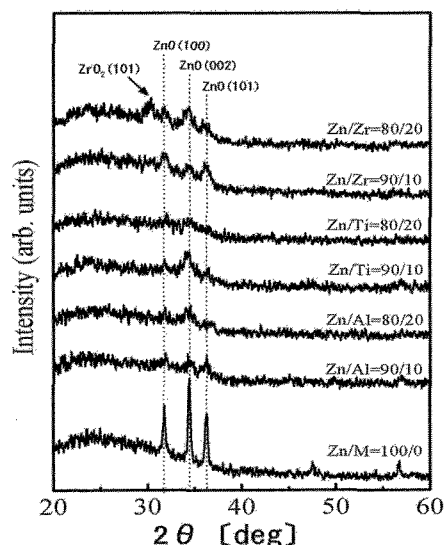


Fig. 3 XRD patterns of ZnO-MO_x films fired at 500°C.

3.3 Microstructure of ZnO-MO_x films

Fig. 4 shows SEM photographs for the surface of ZnO-MO_x films fired at 500°C. The corrugate structure and cracks were observed with the size from 5 to 30 μm in ZnO(100/0) film. Therefore, the resultant film was translucent. The grain size of ZnO film was in the range from 50 to 100 nm and pores existed at the grain boundaries.

The corrugate structure and cracks were observed in ZnO-AlO_{1.5} (90/10) film same as ZnO (100/0) film. The surface of (80/20) film was flat compared with (90/10) film but crack existed. The grain size of (90/10) film was smaller than (100/0) film. The grain size of (80/20) film was larger than that of (90/10) film.

In ZnO-TiO₂ (90/10) film, the corrugate structure and cracks were observed with the size from 1 to 5 μm. The size of corrugate structure in ZnO-TiO₂ (80/20) film (0.3~0.5 μm) further decreased with increasing of Ti content. The grain size of (90/10) film as well as (80/20) film was small (20~30nm). The (80/20) film was transparent but cracks existed.

In ZnO-ZrO₂ (90/10) film, cracks were observed same as ZnO-AlO_{1.5} (90/10) and ZnO-TiO₂ (90/10). The grain size of ZnO-ZrO₂ (80/20) film was larger than that of (90/10). The film thicknesses of the (80/20) was 700 nm as shown in the cross-section image of the film (Fig. 4(h)). As a result, only ZnO-ZrO₂ (80/20) was crack free film.

3.4 Optical property of ZnO-MO_x films

Fig. 5 shows optical transmittance spectra of ZnO-MO_x films. ZnO (100/0) film exhibited low transmittance in the visible region due to the corrugate structure and crack in the film surface. In ZnO-AlO_{1.5}, (90/10) film exhibited low transmittance in visible region same as ZnO (100/0) film. The (80/20) film exhibited high transmittance in visible region and high UV shielding property. However, cracks were observed in the film.

In ZnO-TiO₂, the appearance of (90/10) film was translucent, therefore transmittance in visible region was lower than transparent film such as (80/20). The UV shielding property of (90/10) film was higher than (80/20) film. This result agreed with the difference of crystallinity measured by XRD.

In contrast, the ZnO-ZrO₂ (80/20) film exhibited higher transmittance in the visible region (>90%), and lower transmittance in the UV region (<10%).

4. CONCLUSIONS

The precursor solutions for the preparation of ZnO-MO_x films were synthesized by the reaction between zinc acetate, metal alkoxide and monoethanolamine in 1-propanol solvent. Particularly, the addition of zirconium component in ZnO film improved the microstructure of the film surface. The higher crystallinity was obtained in ZnO-ZrO₂ (80/20) film compared with other ZnO-MO_x films. As a result, ZnO-ZrO₂ (80/20) film with higher transmittance in the visible region ($T_{VIS}>90\%$) and higher shielding property in the ultraviolet region ($T_{UV}<10\%$) was successfully deposited by only one dip coating operation, followed by the firing at 500°C.

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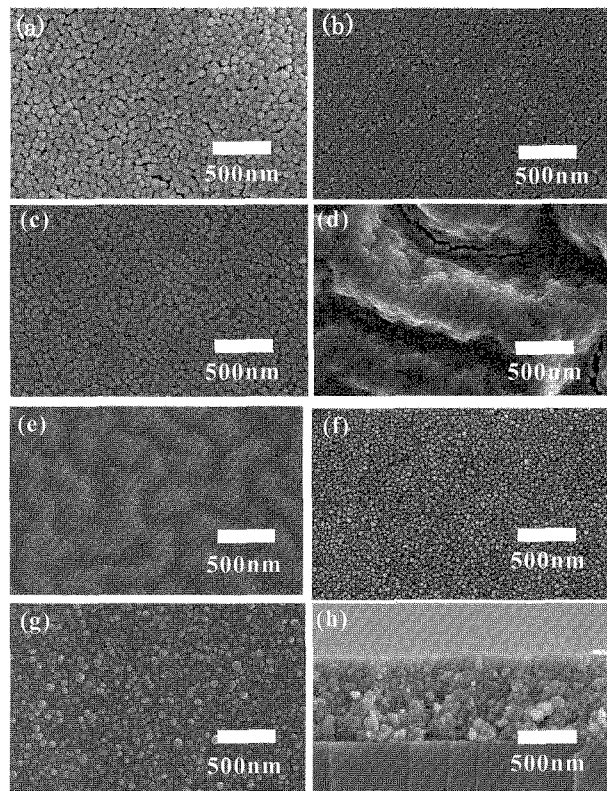


Fig. 4 SEM micrographs of the surface of ZnO-MO_x films (a)ZnO, (b)Zn/Al=90/10, (c)Zn/Al=80/20, (d)Zn/Ti=90/10, (e)Zn/Ti=80/20, (f)Zn/Zr=90/10, (g)Zn/Zr=80/20 and cross section (h)Zn/Zr=80/20.

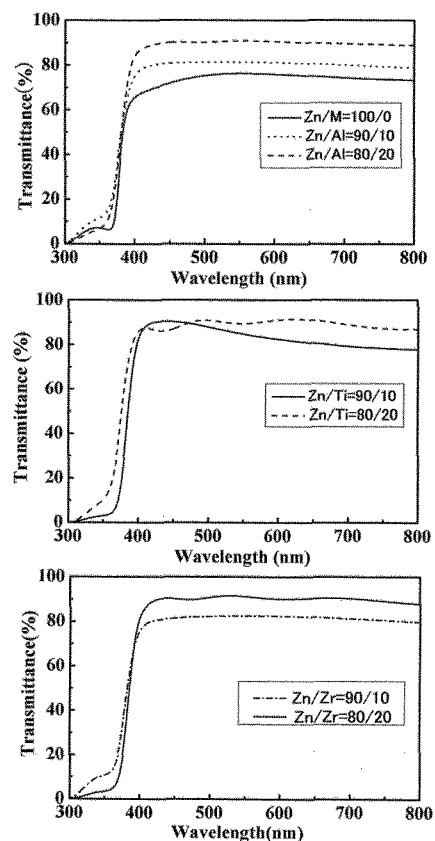


Fig. 5 UV-VIS spectra of ZnO-MO_x films.