

ZnO–ZrO₂ films with good UV-shielding properties prepared by a single step sol–gel method

Hiroaki HAYASHI,^{*,**,*†} Osamu YOSHIDA^{*} and Hisao SUZUKI^{**}

^{*}Research and Development Center, Tsuchiya Co., Ltd., 22-4 Higashinamiki-kita, Yamamachi, Chiryu, Aichi 472-0006

^{**}Graduate School of Science and Technology, Shizuoka University, 3-5-1 Johoku, Hamamatsu, Shizuoka 432-8561

This paper describes a single step sol–gel method, which is very useful for the manufacturing of various films. In this paper, ZnO–ZrO₂ films with excellent ultraviolet ray shielding property were fabricated by a single step deposition of sol–gel spin coating. Zinc acetate dihydrate [Zn(OCOCH₃)₂·2H₂O] and zirconium n-propoxide [Zr(OC₃H₇)₄] were used as starting materials. Monoethanolamine was added to dissolve zinc acetate in alcoholic solvent. Precursor solution with the molar ratio of [Zn]/[Zr] from 100/0 to 60/40 were prepared for the deposition. The effects of zirconium addition on the stability of the precursor solution, crystallization behavior of ZnO–ZrO₂ film, optical property and microstructure were examined. As a result, the stability of the precursor solution increased with increasing ZrO₂ content. Dried films with zirconia component were more stable to humidity in air than the films without zirconia. The addition of zirconia component to the ZnO film also improved the microstructure of the film surface. Namely, the surface of the film with the molar ratio [Zn]/[Zr] of 70/30 became flat without crack. Relatively thick ZnO–ZrO₂ film with thickness about 0.7 μm was obtained by the single step deposition. The resultant film with a [Zn]/[Zr] of 70/30 exhibited high transmittance in the visible region (T_{VIS}~90%) and low transmittance in the ultraviolet region (T_{UV} < 10%). This suggested that the ZnO–ZrO₂ film with good UV-shielding property was successfully prepared by a single step sol–gel spin coating.

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1. Introduction

Zinc oxide (ZnO) is widely used in various applications such as transparent conductive film,^{1,2)} acoustic wave devices,³⁾ laser,⁴⁾ gas sensor,⁵⁾ solar cell,⁶⁾ blue and ultraviolet (UV) light emitters⁷⁾ and UV ray shielding agent.⁸⁾ UV shielding coatings for automotive windows and headlamp lens should exhibit high transmittance in the visible region and high absorbance in the UV region. From the viewpoint of this, ZnO is a suitable material for the UV shielding coatings because of its wide direct band gap of 3.3 eV.

ZnO films have been prepared by various methods such as sputtering,⁹⁾ chemical vapor deposition (CVD),¹⁰⁾ plasma assisted molecular beam epitaxy,¹¹⁾ pulsed laser deposition (PLD),¹²⁾ spray pyrolysis¹³⁾ and sol–gel method.¹⁴⁾ Among them, the sol–gel method is more useful and cost effective. Therefore, many researchers have reported the deposition of the sol–gel derived ZnO film, using zinc acetate dihydrate as a Zn source and monoethanolamine as a stabilizer of the precursor solution.^{15)–17)} In their cases, however, multi-step deposition was essential to obtain the desired film thickness, usually 5 to 10 times coating and drying operations. If the thick films could be deposited by a single step coating via the sol–gel method, it is very useful for the industries. Recently, a single step coating of a relatively thick film by the sol–gel method has been reported.¹⁸⁾ In this paper, anhydrous zinc acetate was used to avoid the introduction of large amounts of water in the precursor solution. However, the maximum thickness of ZnO film was 437 nm. The

transmittance in UV region and visible region were higher than 10% and lower than 85%, respectively. Generally, it has been required that the transmittance of UV region and visible region for the UV shielding film of automotive applications are lower than 10% and higher than 90%, respectively. Therefore, thicker ZnO film is essential for the film with good UV shielding property. In order to obtain the thick film by a single step sol–gel coating process, a stable precursor solution is necessary to avoid the precipitation by humidity in atmosphere.

In this study, we report the preparation of the ZnO–ZrO₂ films with good UV-shielding properties by a single step coating process. This paper describes the effects of the ZrO₂ addition on the stability of the ZnO–ZrO₂ precursor solution, crystallization behavior of the resultant ZnO–ZrO₂ film, microstructure and their optical properties.

2. Experimental Procedure

2.1 Preparation of ZnO–ZrO₂ precursor solution and the film from the solution

ZnO–ZrO₂ thick film was prepared by sol–gel method. **Figure 1** shows the flow diagram for the preparation of ZnO–ZrO₂ precursor solution and the ZnO–ZrO₂ film.

Zinc acetate dihydrate (Zn(OCOCH₃)₂·2H₂O, Wako Pure Chemical Industries, Ltd.; ZnAc) and zirconium n-propoxide (Zr(n-OC₃H₇)₄, 70% in 1-propanol, Kishida Chemical Co., Ltd.; ZrPr) were used as Zn and Zr sources, respectively. 1-propanol (nPA) was used as a solvent. ZrPr was diluted in nPA at room temperature, followed by the addition of monoethanolamine (MEA) into the solution. After that, ZnAc was dissolved in the solution at 60°C. Poly-vinyl pyrrolidone (PVP) was added in the solution as thickening agent. The molar ratio, [Zn]/[Zr] was var-

[†] Corresponding author: H. Hayashi; E-mail: hhayashi@tsuchiya-group.co.jp

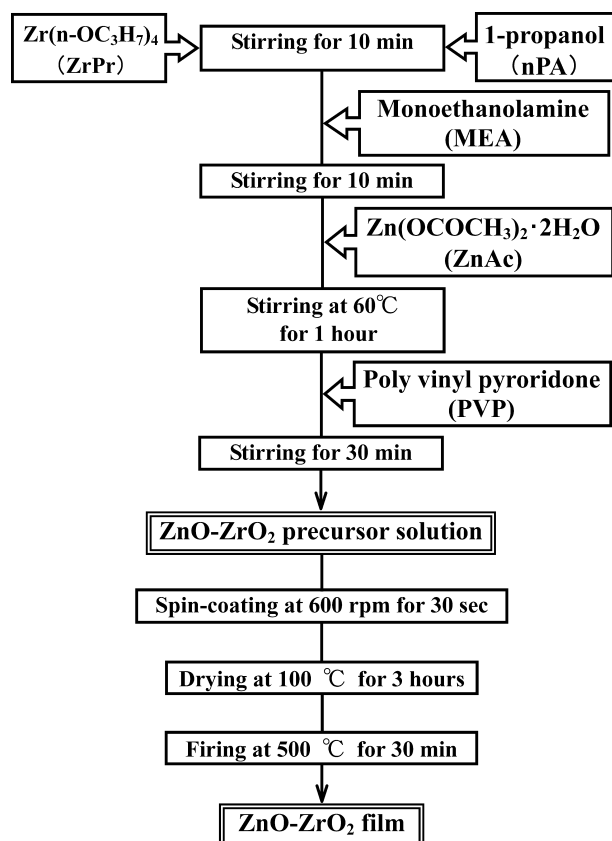


Fig. 1. Flow diagram for the preparation of ZnO–ZrO₂ precursor solution and single step deposition from the solution.

ied 100/0, 90/10, 80/20, 70/30 and 60/40. The concentration of zinc acetate was fixed at 1 M. The molar ratio, [MEA]/([Zn] + [Zr]) was fixed at 0.72. The amount of PVP to 1-propanol was maintained at 1 mass%.

ZnO–ZrO₂ film was deposited on a soda lime glass substrate by spin coating. The precursor solution was dropped onto the substrate and rotated at 600 rpm for 30 s. After the spin coating, the film was dried at 100°C for 3 h. The film was then fired at 500°C for 30 min.

2.2 Characterization

The thermal decomposition behavior of ZnO–ZrO₂ precursor gels were measured by thermo-gravimeter / differential thermal analyzer (TG/DTA, EXSTER6300 Seiko Instrument Inc.) with a heating rate of 10°C/min. The ZnO–ZrO₂ precursor gel films were prepared by drying the precursor solution at 100°C. Crystalline phases in the films were identified by X-ray diffraction (XRD, RINT2000 Rigaku Co.) using Cu K α radiation. Surface and cross-sectional morphologies of the films were observed by a field emission-type scanning electron microscope (FE–SEM, S–4700 Hitachi, Ltd.). UV-VIS transmittance measurements were carried out using an ultraviolet-visible spectrophotometer (UV-VIS, U–4000 Hitachi, Ltd.).

3. Results and discussion

3.1 Stability of the ZnO–ZrO₂ precursor solution

Table 1 shows the change in appearance of the ZnO–ZrO₂ precursor solution with the storage time at room temperature. Every as prepared solution was clear just after the preparation. However, precipitation occurred within six months in the precu-

Table 1. Appearance of ZnO–ZrO₂ Precursor Solutions with Various Ratios of [Zn]/[Zr]

Zn/Zr	As prepared	After 3 months	After 6 months
100/0	○	×	×
90/10	○	×	×
80/20	○	○	×
70/30	○	○	○
60/40	○	○	○

○: Clear solution, ×: Precipitate

Table 2. Appearance of ZnO–ZrO₂ Drying Films and Firing Films

Zn/Zr	Drying at 100°C	Firing at 500°C
100/0	△	×
90/10	○	×
80/20	○	○
70/30	○	○
60/40	○	○

○: Transparent, △: Translucent, ×: Crack

sor solution with [Zn]/[Zr] of 100/0, 90/10 and 80/20. With increasing ZrO₂ content, the stability of the precursor solution increased. The precursor solutions with [Zn]/[Zr] of 70/30 and 60/40 were clear over the six months. The stable solution could be obtained by addition of zirconium propoxide even in high zinc concentration of 1 M. These results suggested that zirconium n-propoxide reacted with zinc acetate and monoethanolamine to form more soluble and stable precursor in 1-propanol solvent.

3.2 The appearance of the ZnO–ZrO₂ films

Table 2 shows the appearance of the ZnO–ZrO₂ films derived from the precursor solution. Only the dried film of ZnO became cloudy, and the other dried films with [Zn]/[Zr] of 90/10, 80/20, 70/30 and 60/40 were transparent. The resulting films with zirconia component were more stable to humidity in air than the films without zirconia. Transparency of the dried films increased with increasing Zr addition. These results show that Zr addition is effective to form a stable precursor gel film. After firing at 500°C, cracks occurred in films with [Zn]/[Zr] of 100/0 and 90/10. Other films with [Zn]/[Zr] of 80/20, 70/30 and 60/40 were transparent and no crack.

3.3 Thermal decomposition behavior of ZnO–ZrO₂ gels

Figure 2 shows the DTA curves for the ZnO–ZrO₂ dried gels. In the DTA curve of ZnO gel, three small and one large exothermic peaks were observed at around 175°C, 248°C, 305°C and 373°C, respectively. The first three peaks may be due to the combustion of MEA and other residual organics. The large exothermic peak at around 373°C is associated with the formation of ZnO.¹⁹⁾ In the case of ZnO–ZrO₂ precursor gel with [Zn]/[Zr] of 80/20, the large exothermic peak at around 380°C was observed. The films with zirconia component exhibited the higher peak temperature than ZnO gel. Moreover, a new exothermic peak was observed around 410°C. The peak is associated with the formation of ZrO₂. In the precursor gel with [Zn]/[Zr] of 60/40, two large exothermic peaks, corresponding to the for-

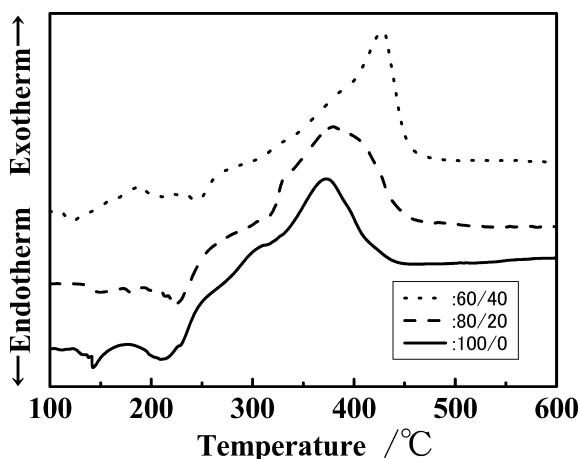


Fig. 2. DTA curves of ZnO–ZrO₂ gels with various ratios of [Zn]/[Zr].

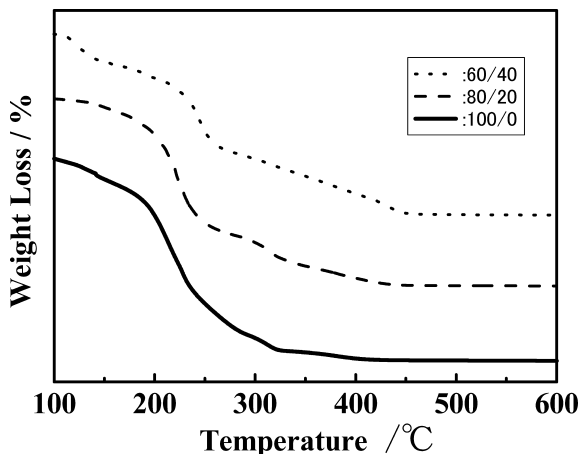


Fig. 3. TG curves of ZnO–ZrO₂ gels with various ratios of [Zn]/[Zr].

mation of ZnO and ZrO₂ appeared around 385°C and 428°C, respectively. With increase in zirconium content of the precursor gel, both temperatures of exothermic peaks increased. These results also suggested that more stable precursor was formed by addition of zirconium alkoxide. **Figure 3** shows the TG curves of ZnO–ZrO₂ gels. In ZnO gel, weight loss was observed in four temperature regions of 100–180°C, 180–230°C, 230–320°C and 320–425°C. Similarly, in the case of the gel with the molar ratio [Zn]/[Zr] of 80/20, four temperature region of weight loss was observed, but the temperature region shifted to higher temperature such as 100–190°C, 190–250°C, 250–325°C and 325–440°C. Further, in the case of the gel with the molar ratio [Zn]/[Zr] of 60/40, the temperature region of weight loss increased such as 100–220°C, 220–260°C, 260–420°C and 420–450°C. These results also indicated that increasing amount of zirconium alkoxide resulted in the more stable ZnO–ZrO₂ precursor solutions. Comparing TG curves of the gels with the molar ratio [Zn]/[Zr] of 100/0, 80/20 and 60/40, the weight loss in each similar temperature region decreased with increase in ZrO₂ content. The rapid weight loss during firing causes the crack in the film. Therefore, the addition of ZrO₂ in the precursor film containing ZrO₂ is suitable to avoid the crack among the firing.

3.4 Crystallization of ZnO–ZrO₂ films

Figure 4 shows XRD patterns for the ZnO–ZrO₂ films with

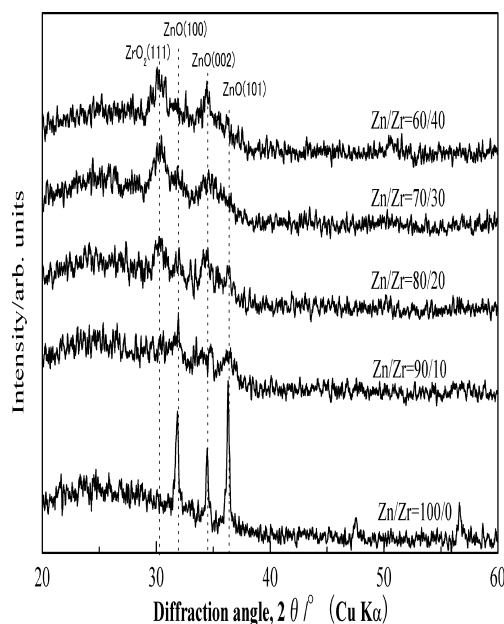


Fig. 4. XRD patterns of ZnO–ZrO₂ films with various ratios of [Zn]/[Zr] fired at 500°C

different compositions fired at 500°C. The XRD pattern of ZnO film exhibited three main sharp peaks corresponding to the (100), (002), and (101) planes of the ZnO wurzite structure. The intensities of XRD peaks corresponding to ZnO decreased dramatically with increasing ZrO₂ content, while the intensity corresponding to the (111) plane of tetragonal ZrO₂ increased with increasing ZrO₂ content. The width of the peaks corresponding to ZnO increased with increasing ZrO₂ content in the film. These results exhibited that the crystallinity and the grain size of ZnO decreased with increasing ZrO₂ content. The result of decrease in the crystallinity was supported by the results of DTA / TG; the temperature corresponding to the formation of ZnO increased with increasing ZrO₂ content. The orientation of ZnO phase changed with ZrO₂ content in the film. The (101) peak was the strongest in ZnO film. The (100) peak was the strongest in the film with the molar ratio of 90/10. More addition of ZrO₂ resulted in the gradually oriented film in the c-axis, or (002) plane such as the films with the molar ratio [Zn]/[Zr] of 70/30 and 60/40.

3.5 Microstructures of ZnO–ZrO₂ films

Figure 5 shows SEM photographs for the surface of ZnO film fired at 500°C. The corrugate structure and cracks were observed in the range from 5 to 30 μm. The film was translucent because of its microstructure. The grain size of ZnO film was 50–100 nm and pores existed at the grain boundaries. **Figure 6** shows SEM photographs for the surface and the cross section of the film with the molar ratio [Zn]/[Zr] of 70/30. The surface of the film was flat without crack. The grain size of the film was small (20–80 nm) compared with that of the ZnO film. The addition of ZrO₂ resulted in the control of grain growth in the film. These results showed the good agreement with the results of XRD; the grain size of ZnO in the film decreased with increasing ZrO₂ content. The thickness of the film with the molar ratio [Zn]/[Zr] of 70/30 was 700 nm. Relatively thick and crack free film was obtained by a single step coating. This fact is probably due to the stress relaxation by the residual amorphous phase in the film on firing. Therefore, even relatively thick film could avoid the crack in the

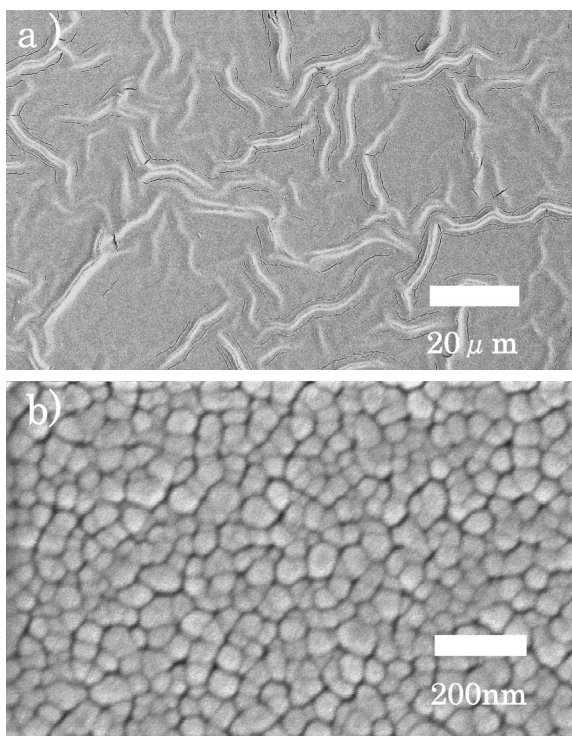


Fig. 5. SEM photographs for the surface of a ZnO film, a) low magnification image and b) high magnification image.

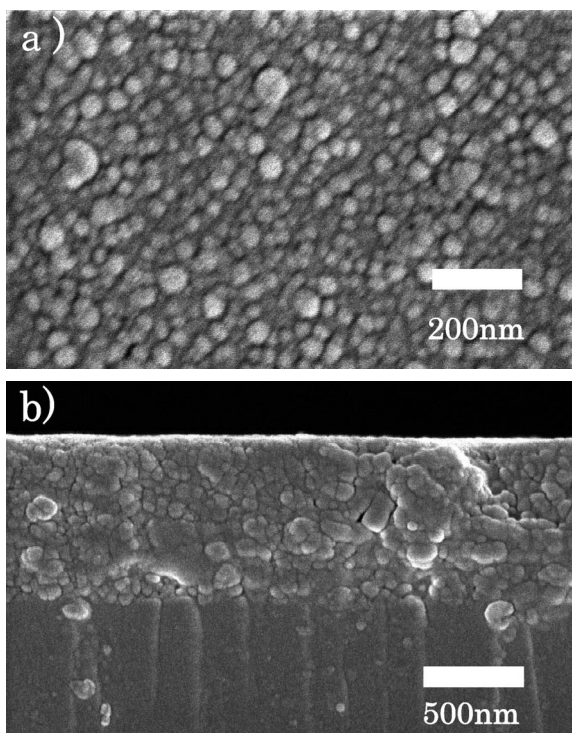


Fig. 6. SEM photographs for a) the surface and b) cross section of a ZnO-ZrO₂ film with the molar ratio [Zn]/[Zr] of 70/30.

film among firing.

3.6 Optical property of ZnO-ZrO₂ films

Figure 7 shows optical transmittance spectra of ZnO-ZrO₂

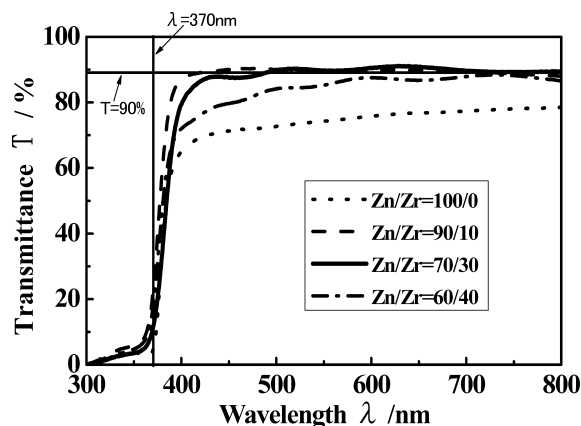


Fig. 7. UV-VIS spectra for ZnO-ZrO₂ films with various ratios of [Zn]/[Zr] fired at 500°C.

films. The ZnO film exhibited low transmittance in the visible region because of the corrugate structure and crack in the film surface. The transmittance in visible region was improved by addition of ZrO₂. The film with the molar ratio [Zn]/[Zr] of 90/10 had high transmittance in the visible region ($T_{\text{vis}} \sim 90\%$). However, when ZrO₂ or zirconium source was added to the precursor solutions more than 20%, the transmittance of the film in visible region slightly decreased. This result is ascribed to the refractive index of the film with increasing ZrO₂ content. The transmittance in UV region (wave length < 370 nm) of the films with the molar ratio [Zn]/[Zr] of 100/0 and 70/30 were lower than 10%. Only the film with the molar ratio [Zn]/[Zr] of 70/30 exhibited high transmittance in the visible region and low transmittance in the ultraviolet region by a single step coating through the sol-gel process.

4. Conclusions

The precursor solutions for the deposition of ZnO-ZrO₂ film were synthesized by reacting with zinc acetate, zirconium propoxide and monoethanolamine in 1-propanol solvent. The molar ratio of [Zn]/[Zr] was varied from 100/0 to 60/40. The effects of zirconia addition on the stability of the solution, crystallization behavior of ZnO-ZrO₂ films, microstructure and their optical properties have been investigated. With increasing ZrO₂ content, the stability of the precursor solution increased. Precipitation did not occur in the precursor solution with the molar ratio [Zn]/[Zr] of 70/30 and 60/40 over the six months. The intensities of XRD peaks corresponding to ZnO decreased sharply with increasing ZrO₂ content in the film, while the intensity of the peak corresponding to (111) plane of tetragonal ZrO₂ increased with increasing ZrO₂ content. The grain size of the film decreased with increasing ZrO₂ content. The addition of ZrO₂ in the film also improved the microstructure of the film surface. The surface of the film with the molar ratio [Zn]/[Zr] of 70/30 was flat without crack. The grain size of the film was small (20–80 nm) if compared with that of ZnO film. The addition of ZrO₂ resulted in the suppression of the grain growth in the film. ZnO-ZrO₂ film with the molar ratio [Zn]/[Zr] of 70/30 exhibited high transmittance in the visible region ($\sim 90\%$) and low transmittance in the ultraviolet region (< 10%). The film was successfully obtained by a single step sol-gel spin coating, followed by the firing at 500°C.

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