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# Synthesis and optical properties of ZnO thin films prepared by SILAR method with ethylene glycol

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**Abstract.** An ultrasonic-mediated assisted stepwise method has been developed for depositing transparent ZnO films from aqueous solution. Rinsing in low ethylene glycol temperature was easy to produce intermediate phase of $Zn(OH)_2$, rinsing in 120℃ ethylene glycol was observed the diffraction peak of intermediate $Zn(OH)_2$ in early report, the rinsing temperature plays an important role in the process of $Zn(OH)_2$ phase transformed to ZnO, high rinsing temperature actually improved the intermediate phase. However, the effect of rinsing on the intermediate phase is yet to be understood clearly. The effect of different rinsing procedures, involving either of or a combination of successive ionic layer adsorption and reaction (SILAR) and ultrasonic-assisted rinsing, prior to hydrolysis in ethylene glycol was investigated to deposit ZnO thin films. Ultrasonic-assisted rinsing process before hydrolysis in ethylene glycol was found to improve the occurrence $Zn(OH)_2$ in ZnO thin films. In the zinc complex ($[Zn(NH_3)_4]^{2+}$) solution, excess ($[Zn(NH_3)_4]^{2+}$) absorbed in glass substrate transformed incompletely to ZnO and exist as $Zn(OH)_2$ phase in thin films. In films deposited at low temperature, rinsing procedure is applied to improve excess $Zn(OH)_2$ and obtain smoother transparent thin films.

**Keywords:** SILAR; ZnO thin films; ethylene glycol

## 1. Introduction

ZnO, an important semiconductor material, has a large band gap ($E_g$ = 3.37 eV) and crystallizes in hexagonal wurtzite structure ($c$ = 0.521 nm, $a$ = 0.325 nm) with oxygen atoms on hexagonal sites and zinc atoms on tetrahedral sites. ZnO possesses good optical characteristics, high stability, and excellent electrical properties. Since ZnO has a wide band gap, a low power threshold for optical pumping at room temperature, and exhibits UV emission, resulting from a large exciton binding energy of 60 meV, it can be used in light emitting diodes (LEDs), solar cells, photo detectors, electroluminescent devices and next-generation UV lasers. In addition, ZnO films with high transmittance in visible spectrum and low resistivity are suitable as transparent electrodes for displays.

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ZnO thin films have been prepared by various chemical and physical deposition techniques such as sputtering, pulsed laser ablation, successive ionic layer adsorption and reaction (SILAR) (Gao *et al.* 2004, Gao *et al.* 2004, Gao *et al.* 2007, Jimenez-Gonzailez *et al.* 1995, Kumar *et al.* 2011, Lupan *et al.* 2008, Lupan *et al.* 2009, Shishiyanu *et al.* 2005, Vargas-Hernandez *et al.* 2008), sol-gel (Habibia and Sardashtia 2008, Jain *et al.* 2007, Li *et al.* 2005), chemical bath deposition (CBD) (Drici *et al.* 2004, Miyazaki *et al.* 2006, Yamada *et al.* 2005), and chemical vapor deposition (CVD) (Sun *et al.* 2008)**.** Among them, the solution approached based on the chemical technique has attracted increasing attention in recent years owing to its relatively low temperature requirement, low cost, high reliability, and ability to deposit films over large areas. However, very little effort has been devoted to the fabrication of transparent ZnO films via the SILAR method. Gao *et al.* (2004) have integrated ultrasonic rinsing into the SILAR process for the preparation of ZnO thin films. In a previous report by Shei *et al.* (2011), our group investigated the difference in film properties obtained using deionized (DI) water and ethylene glycol rinsing procedures. Moreover, ultrasonication in addition to the rinsing improves the ZnO film quality and yields higher optical transmittance (>90%). However, in another report of Gao and coworkers on the temperature effect on ethylene glycol rinsing, the film was not transparent as previously reported. In this case, the ultrasonication was carried out after hydrolysis in ethylene glycol, and the rinsing process is different from that employed in our previous report (Shei *et al.* 2011). In order to clarify the effect of rinsing on ethylene glycol deposition, different rinsing procedures were employed before hydrolysis and results are discussed.

In this study, we investigated how the quality of ZnO thin films was affected by various rinsing processes performed before hydrolysis in ethylene glycol. ZnO thin films integrated the ultrasonic-assisted by SILAR methods, despite its simple procedure and fast growth rate, the film exhibited relatively low transmittance (80%). The process of precursor adsorption onto the substrate was important for thin film deposition. Excess absorption caused an intermediate phase of $Zn(OH)_2$ to remain in the thin films at low temperature. Additional rinsing reduced the amount of intermediate phase and increased the transmittance from 80% to 90%.

## 2. Experimental

ZnO thin films were deposited on glass substrates by the SILAR method. In the experiments, 0.1 M $ZnCl_2$ and concentrated 29% ammonia ($NH_4OH$) were used to prepare the solution of zinc complex ([ $Zn(NH_3)_4]^{2+}$). $NH_4OH$ was added to adjust the pH of the solution to 10. Each ZnO film sample was grown by 20 cycles of deposition prior to testing of its crystallinity and microstructure. In SILAR depositions of ZnO thin films, three rinsing procedures are discussed. These were named Rinsing Procedures 1, 2, and 3. Detailed procedures for one cycle of ZnO film deposition are shown in Fig. 1 and described as follows:

(1) Rinsing Procedure 1

a. Dip glass substrates in the zinc complex ($[Zn(NH_3)_4]^{2+}$) solution for 20 s.

b. Dip glass substrates in heated ethylene glycol for 20 s. A precipitate of $Zn(OH)_2$ is formed and then transformed to a ZnO film.

c. Keep substrates in ultrasonic-assisted DI water for 30 s to remove loosely attached ZnO and unreacted Zn $(OH)_2$ grains.

(2) Rinsing Procedure 2

a. Dip glass substrates in zinc complex ($[Zn(NH_3)_4]^{2+}$) solution for 20 s.

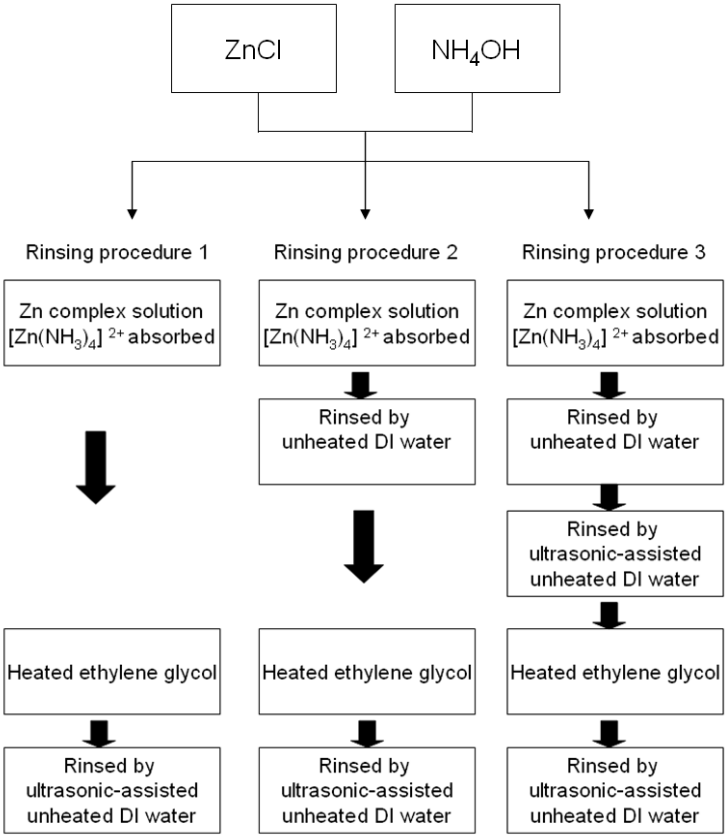


Fig. 1 Schematic of rinsing procedures for the deposition of ZnO thin films

b. Dip substrates in unheated DI water for 20 s. $Zn(OH)_2$ precipitation occurs on the substrates.

c. Dip glass substrates in heated ethylene glycol and reaction for 20 s to form ZnO.

d. Keep substrates in ultrasonic-assisted DI water for 30 s to remove loosely attached ZnO and unreacted Zn $(OH)_2$ grains.

(3) Rinsing Procedure 3

a. Dip glass substrates in the solution of zinc complex ($[Zn(NH_3)_4]^{2+}$) for 20 s.

b. Dip substrates in unheated DI water for 20 s. $Zn(OH)_2$ precipitation occurs on the substrates.

c. Dip glass substrates in ultrasonic assisted DI water for 30 s to remove $Cl^-$ counterions and loosely attached $Zn(OH)_2$ grains.

d. Dip glass substrates in heated ethylene glycol and allow them to react for 20 s to form ZnO.

e. Keep substrates in ultrasonic-assisted DI water for 30 s to remove loosely attached ZnO and unreacted Zn $(OH)_2$ grains.

Each rinsing procedure was performed at three deposition temperatures, where the temperature of ethylene glycol was 120℃, 150℃, or 180℃)

The reactions occurring in the corresponding procedure are given in Eqs. (1) to (4)

$$Zn^{2+} + 4NH_4OH \rightarrow [Zn\ (NH_3)\ _4]^{2+} + 4\ H_2O \quad (1)$$

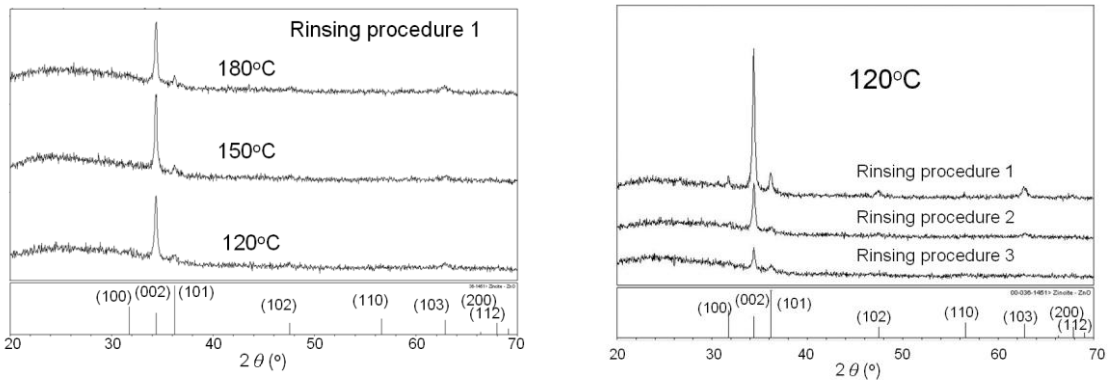


Fig. 2 XRD patterns of ZnO thin films grown at (a) different rinsing temperature and (b) at 120℃ by three rinsing procedures

$$[Zn(NH_3)_4]^{2+} + 4H_2O \rightarrow Zn^{2+} + 4NH_4^{+} + 4OH^{-} \quad (2)$$

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2\,(s) \quad (3)$$

$$Zn(OH)_2 \rightarrow ZnO\,(s) + H_2O \quad (4)$$

Repeating each rinsing procedure for 20 cycles yielded ZnO thin films deposited on glass. Samples obtained using Rinsing Procedure 1, 2, and 3 were labeled as Samples 1, 2, and 3, respectively. A schematic detailing a typical cycle of ZnO film deposition is illustrated in Fig. 1. The structure and microcrystallite size of the films were investigated by X-ray diffraction (XRD). The surface morphology of the samples was examined using scanning electron microscopy (SEM). The optical properties of the ZnO thin films were characterized using an ultraviolet-visible/near infrared (UV-VIS/NIR) spectrophotometer, as well as photoluminescence (PL) and X-ray photoemission spectrometry (XPS).

## 3. Results and discussion

The crystal structure and orientation of the ZnO thin films were investigated by XRD. Fig. 2(a) shows the XRD spectra for ZnO thin films deposited for 20 cycles by Rinsing Procedure 1 at 120, 150, and 180℃. XRD diffraction peaks corresponding to (002) and (101) planes were observed in all ZnO films. The thin films deposited at three different temperatures exhibit peaks corresponding to the (002) plane of wurzite ZnO, located around the diffraction angle ($2\theta$) of 34.42° in XRD patterns. All of the samples exhibited intense peaks corresponding to the (002) plane, indicating preferential orientation along the c-axis. Thin films deposited at 120℃ with a weak peak at 9.41° was detected, it means the presence of intermediate $Zn(OH)_2$ in thin film (Gao *et al.* 2004). In this case, the peak at 9.41° was not detected in the 2θ range 5-15°.

Fig. 2(b) shows the XRD patterns of ZnO thin films deposited by the three rinsing Procedures at 120℃ for 20 cycles. Thin films deposited at the three different temperatures also exhibit peak corresponding to (002) plane, indicating preferential growth along c-axis. The intensity of the diffraction peak corresponding to the (002) plane is related to the film thickness. The thickness of

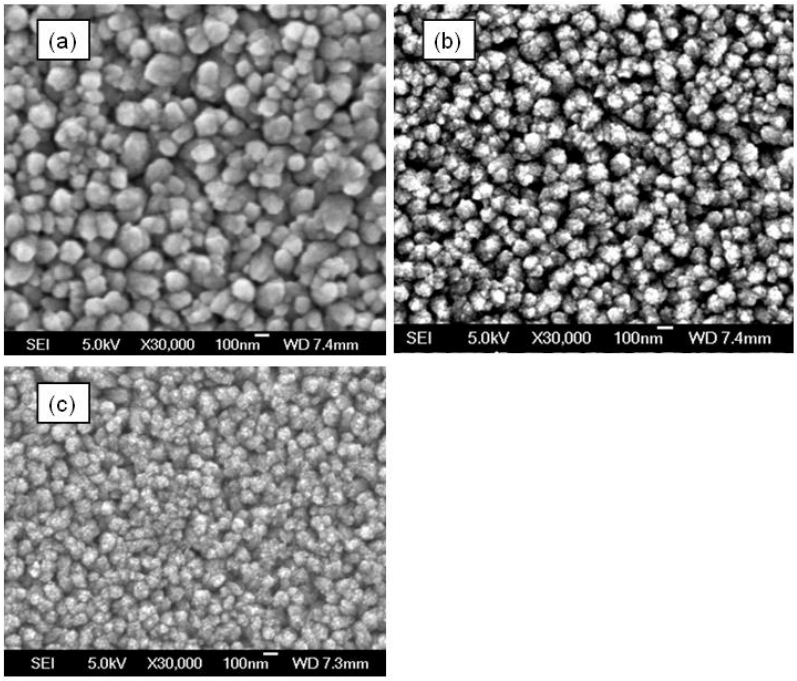


Fig. 3 SEM images of ZnO thin films after 20 cycles of deposition at 120℃ by three rinsing procedures

the films deposited by Rinsing Procedures 1, 2, and 3 are 700, 224, and 203 nm, respectively. To evaluate the mean grain size (D) of the films based on the XRD results, we used Scherrer's formula, $D = 0.94\lambda / B\cos\theta$, where $\lambda$, $B$, and $u$, correspond to $X$-ray wavelength (0.15418 nm), the FWHM of ZnO (002) diffraction peak, and the Bragg diffraction angle, respectively. The values of FWHM for the (002) diffraction peaks of ZnO films deposited by Rinsing Procedures 1, 2, and 3 are 0.228°, 0.270°, and 0.290°. The FWHM of the (002) diffraction peak is routinely used to determine $D$ (using the Scherrer formula) of thin films. The grain size of films deposited by Rinsing Procedures 1, 2, and 3 was calculated to be 9.54 nm, 7.13 nm, and 6.33 nm, respectively. Grain size decreased with increased rinsing. This effect is illustrated schematically in Fig. 4, where the substrates adsorb $[Zn(NH_3)_4]^{2+}$ and are rinsed by DI water and ultrasonic-assisted DI water process. The rinsing process reduces the adsorption of the zinc complex. Upon subjecting all samples to the same hydrolysis time (20 s) in heated ethylene glycol, the transformation of excess $[Zn(NH_3)_4]^{2+}$ into ZnO is incomplete, leading to a possible intermediate phase of $Zn(OH)_2$ in the thin films. However, the $Zn(OH)_2$ phase was not detected by XRD, contrary to the results reported in Gao *et al.* (2007). This suggests that $Zn(OH)_2$ might exist inside the thin film as an amorphous phase. In order to more accurately verify the effect of rinsing, Photoluminescence (PL) and XPS measurements were utilized.

Fig. 3 shows SEM images for the surface of ZnO thin films prepared by the three rinsing procedures at 120℃. The SEM micrographs of ZnO films with seven different thicknesses showed uniform tightly packed grains whose size increases with the film thickness. Thin films with compact grains were obtained by ethylene glycol deposition, where the average grain size is approximately 100 nm. In Fig. 4, the grain size decreased with increased rinsing. These results are consistent with the trend calculated using Scherrer's formula (Kim *et al.* 2004).

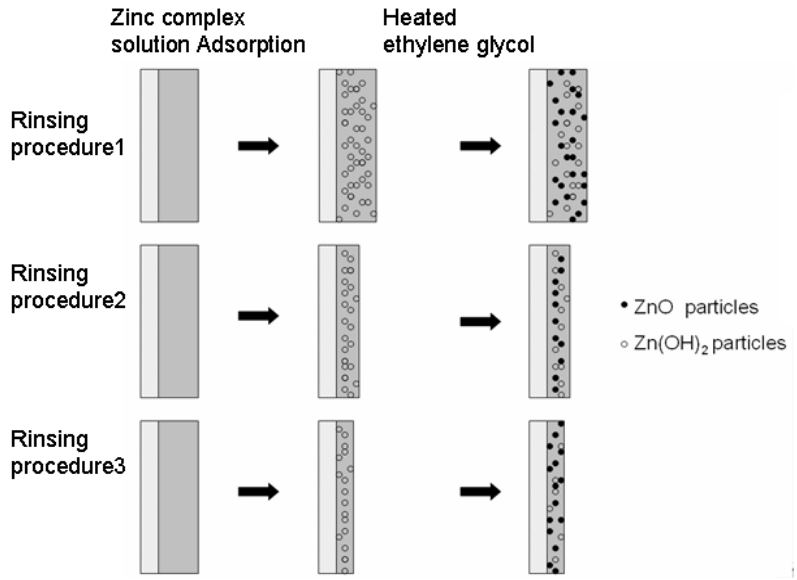


Fig. 4 Schematic thin-film deposition mechanism for the three rinsing procedures

PL spectra can reveal both defects and optical properties of ZnO films, useful for its application as a photonic material. The PL spectra of the ZnO thin films were measured with an excitation wavelength of 325 nm at room temperature to examine the quality of the thin films. The effect of rinsing process on the PL properties of ZnO thin films was investigated. Fig. 5(a) shows the PL spectra of ZnO thin films deposited at different rinsing temperatures. The PL spectra of all samples exhibit two emission peaks, which show UV emission at near band edge and broad green-yellow radiation in the range 485-600 nm. The green-yellow PL intensity significantly decreases with increasing rinsing temperature.

The origin of yellow-green luminescence from ZnO is associated with intrinsic defect centers such as oxygen vacancies ($V_O$), interstitial oxygen ($O_i$), or antisite oxygen ($O_{Zn}$) (Zhao *et al.* 2006, Wang *et al.* 2004). There have been many models proposed to explain the origin of yellow-green emission. It was reported that the luminescence band ranging from 442 to 620 nm in ZnO thin films is related to the presence of $Zn(OH)_2$, which causes emission from the $O_i$ band (543 nm). Since $Zn(OH)_2$ starts to hydrolyze into ZnO and $H_2O$ at 120℃, it was thought that higher temperature would enhance the hydrolysis. In our case, it actually helped to decrease the luminescence intensity of $O_i$ emission band (543 nm). The PL spectra indicate that $O_i$ content of ZnO films increases at low temperature deposition owing to the difficulty in hydrolyzing $Zn(OH)_2$. The role of low temperature in $Zn(OH)_2$ phase formation was reported by Gao *et al.* (2007), from the PL spectra, the tendency of luminescence band ranging from 442 to 620 nm correspond to $Zn(OH)_2$ properties (Zhou *et al.* 2002).

In contrast, Fig. 5(b) shows the PL spectra of thin films deposited at 120℃ by different rinsing processes. Rinsing Procedure 1 led to strong green-yellow PL intensities. Here, it is considered that excess $[Zn(NH_3)_4]^{2+}$ reacted incompletely and the superfluous intermediate phase of $Zn(OH)_2$ affected the PL. Rinsing Procedures 2 and 3 yielded lower growth rate but the additional rinsing reduced the absorption of the zinc complex before the hydrolysis in heated ethylene glycol. The PL properties corresponding to the deposition mechanisms are shown in Fig. 5.

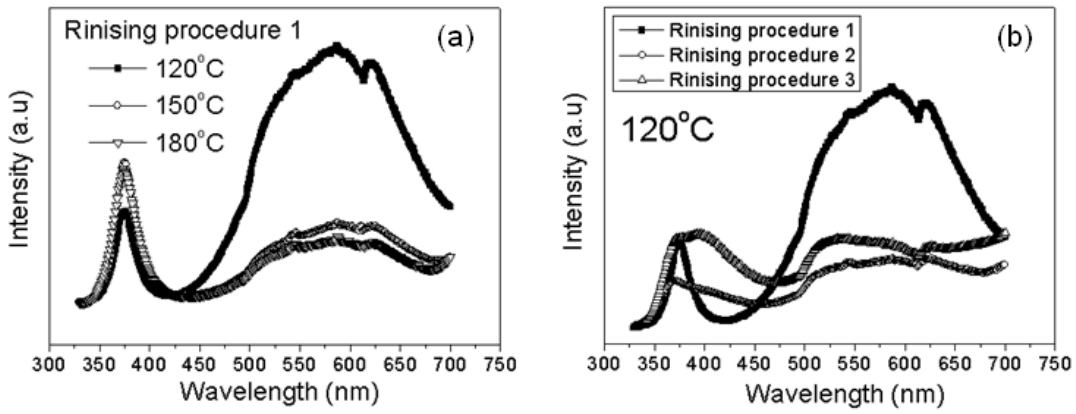


Fig. 5(a) PL spectra of ZnO thin films prepared by 20 cycles of deposition at 120℃, 150℃, and 180℃ using Rinsing Procedure 1. (b) PL spectra of ZnO thin films prepared by 20 cycles of deposition at 120℃ using Rinsing Procedure 1-3

After measuring the PL properties of ZnO films, XPS was applied to identify changes in chemical structure caused by rinsing temperature, in order to locate the $Zn(OH)_2$ phase in the ZnO films. XPS analysis of ZnO thin films prepared at different rinsing temperature was performed to determine the chemical state of the constituent elements in each film. XPS measurement was carried out after the removal by Ar ion etching of the surface layer, more than 50 nm thick, of hydroxyl groups (Zn-OH) adsorbed onto the thin films (Noei *et al.* 2008). Fig. 6 shows the multiplex spectra of the O 1s peak for ZnO thin films grown at different rinsing temperatures. The typical O1s peak in the surface can be consistently fitted by two nearly Gaussian profiles, as shown in Figs. 6(a)-(c). For an as-grown film, the binding energy of the O 1s peak, located around 532.0 eV, is usually attributed to the presence of a $Zn(OH)_2$ phase in ZnO films. Moreover, the binding energies of the O 1s peak in the range 529.7–530.6 eV was reported that the Zn-O bond formation (Takamori *et al.* 2007, Khallaf *et al.* 2009, Jing *et al.* 2002). In Fig. 6(a), ZnO films deposited at 120°C by Procedure 1 exhibited stronger intensity in the peak corresponding to the Zn-OH bond. According to Fig. 6(b), the Zn-OH bond intensity decreased upon additional water rinsing. Fig. 6(c) shows the lowest Zn-OH bond intensity, obtained by water rinsing and ultrasonic-assisted procedure. This result explains the excess $Zn(OH)_2$ in the ZnO film deposited by Procedure 1. Additional rinsing diminishes the absorption of the zinc complex; this helps avoid the formation of surplus intermediate phase in the thin films. Upon increased rinsing, a decrease in peak intensity corresponding to the Zn-OH bond, and an increase in peak intensity corresponding to the Zn-O bond was obtained because of the reduction of the zinc complex absorbed on substrate. The results of XPS measurements are consistent with the previous PL data and verify that $Zn(OH)_2$ actually remains in thin films as an amorphous phase. From these results, the PL and XPS characteristics of ZnO thin films prepared by SILAR are found to be strongly dependent on the rinsing temperature. Rinsing-assisted enhancement for ZnO films after hydrolysis in ethylene glycol was previously reported by Gao *et al.* (2007). In this case, rinsing before hydrolysis in ethylene glycol, during the low temperature deposition of ZnO films was investigated to reduce the amount of excess intermediate phase.

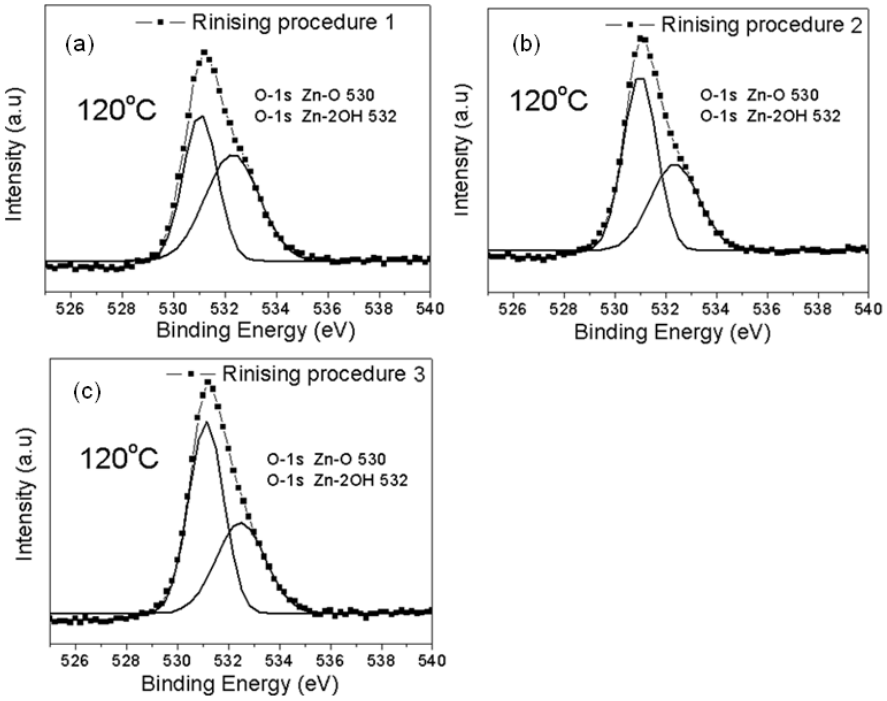


Fig. 6 ZnO XPS multiplex spectra of the O 1s deposited at 120℃ by three rinsing procedures

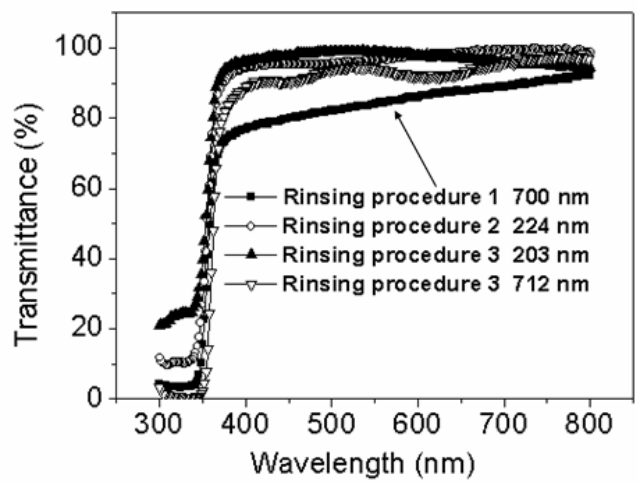


Fig. 7 The optical transmittance spectra of ZnO thin films deposited at 120℃ by different rinsing procedures

Fig. 7 shows the optical transmittance spectra of the ZnO thin films prepared by the three rinsing procedures at 120℃. The film deposited by Rinsing Procedure 1 shows only an average transmittance of 85% in the visible region. The transmittance of ZnO films deposited by Rinsing Procedures 2 and 3 reaches up to 95% in the visible range (400-800 nm). The sharp ultraviolet absorption edges occurred at approximately 350 nm. The transmittance was related to the

thickness, where Procedures 1, 2, and 3 yielded films of thickness 700 nm, 224 nm, and 203 nm, respectively. In order to compare the effect of rinsing on the optical properties of each film, a thin film was deposited in 70 cycles using Procedure 3, yielding a film with a thickness of 712 nm. This thickness is close to that of the thin films deposited in 20 cycles using Procedure 1 (700 nm thick). The transmittance of the thin film deposited by Procedure 3 stayed higher than 90% in the visible region. This was higher than that reported by Gao *et al.* (2007). These results indicate that high-transmittance thin films were obtained by ethylene glycol deposition, as reported by Shei *et al.* (2011). The rinsing process played an important role in determining the optical properties, where the transmittance was related to the rinsing. Gao *et al.* (2007) used sonication after dipping the sample in heated ethylene glycol, to show the effects of deposition temperature and ultrasonic irradiation on the film quality. In this case, the DI water rinsing and ultrasonic assisted DI water process before dipping the sample in heated ethylene glycol decreased the thin film quality; the growth rate decreased but the defect density and optical properties were enhanced.

## 4. Conclusions

Highly transparent and *c*-axis-oriented ZnO films were deposited on glass substrates at a temperature of 120℃ by the SILAR method using three different rinsing procedures. This work compared solution rinsing routes for the deposition of well crystallized and transparent ZnO thin films. The results confirm the literature reports that ethylene glycol is effective as a heating medium in preparing a dense and transparent ZnO film. However, the rinsing process before the reaction in heated ethylene glycol is the key step to obtain transparent ZnO thin films. Excess $Zn(OH)_2$ in some of the thin film samples indicated that hydrolysis is related to temperature, where higher temperature enhanced the transformation of $Zn(OH)_2$ to ZnO, and low temperature deposition caused excess $Zn(OH)_2$ to form. The optical properties of the films were enhanced with additional rinsing before hydrolysis. The additional rinsing decreased the growth rate and grain sizes but aided in the formation of transparent ZnO thin films. As the thin film thickness increased, the transmittance remained high. Since this deposition process yields transparent and compact films, it may be easily extended to the fabrication of solar cell and LED devices.

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