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The Properties of Nanostructured ZnO Thin Film via Sol-Gel Coating

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Summary

This review presents the recent studies on improving the structural, electrical, and optical properties of nanocrystalline ZnO thin film prepared from sol-gel coating for possible applications to photoconductor, UV optoelectronic, integrated sensor, and transparent conducting oxide electrodes. ZnO thin films can be grown on an inexpensive substrate such as glass at relatively low temperature and these films might have many advantages over indium doped SnO_2 and GaN thin films.

Keywords: Nanostructured; ZnO thin film; Sol-gel; Structural properties; Electrical properties; Optical properties

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INTRODUCTION

As far as nanomaterials are concerned, ZnO thin film is one of the candidates which has been attracting attention due to its numerous interesting properties. ZnO is a natural n-type II-VI semiconductor with a wide bandgap of 3.3 eV and a large exciton binding energy of about 60 meV at room temperature. The actual interest of ZnO nanomaterial in chemistry and solid state physics is due to its excellence in electrical and optical properties. So, the possible applications of the ZnO material are particularly in photoconductor, uv optoelectronic, integrated sensor and transparent conducting oxide electrode in many important devices in place of indium doped SnO_2 and GaN materials. Besides, conducting ZnO material is a good infrared reflectors and it can be used as energy efficient windows that require high refractive index and high transmittance in the visible range (Ji et al., 2004; Maiti et al., 2007; Zhou et al., 2007). So far, ZnO material has received considerable attention and it has been spreading out in a good deal of applications. Therefore, the attention will be given to review the parameters that influence the structural, optical and electrical properties of ZnO thin film prepared by sol-gel coating.

SOL-GEL COATING

Sol-gel method is a wet chemical route for the synthesis of colloidal dispersions of oxides which can be altered to powders, fibers, thin films and monoliths as shown in Figure 1 (Suwanboon, 2006). In general, sol-gel method consists of hydrolysis and condensation reactions.

Hydrolysis is a chemical reaction, for which water reacts with a precursor to produce other compounds, for example,

$$M(OEt)_4 + xH_2O \Leftrightarrow M(OEt)_{4-x}(OH)_x + xEtOH \quad .$$

Condensation involves the hydroxo ligand formation via the bridging hydroxyl (M-(μ-OH)-M) or bridging oxygen (M-O-M) bonds depending on the coordination number of M and the acidity of the bridging hydroxyl ligand:

$$M(OEt)_{4-x}(OH)_x + M(OEt)_{4-x}(OH)_x \Leftrightarrow (OEt)_{4-x}(OH)_{x-1}MOM(OEt)_{4-x}(OH)_{x-1} + H_2O \quad .$$

Condensation results in the formation of nanoscale clusters of metal oxides or hydroxides (Guozhong, 2004). However, this review will only focus on the sol-gel coating.

Sol-gel coating is a process of preparation of single or multicomponent oxide coating which may be glass, glass-ceramic or crystalline ceramic depending on the process. Also, the nanomaterials used in modern ceramic and device technology require high purity and facilitate to control over composition and structure. The sol-gel coating is one of the interesting methods because it has many advantages. Examples are as the followings (Bao et al., 1998).

1. The chemical reactants for sol-gel process can be conveniently purified by distillation and crystallization.
2. All starting materials are mixed at the molecular level in the solution so that a high degree of homogeneity of films can be expected.
3. The trace elements in the form of organometallic compounds or soluble organic or inorganic salts can be added to adjust the microstructure or to improve the structural, optical and electrical properties of oxide films.
4. The viscosity, surface tension and concentration of polymeric solution can be easily adjusted.
5. Large-area films of desired composition and thickness can be easily formed on a complex geometry substrate.

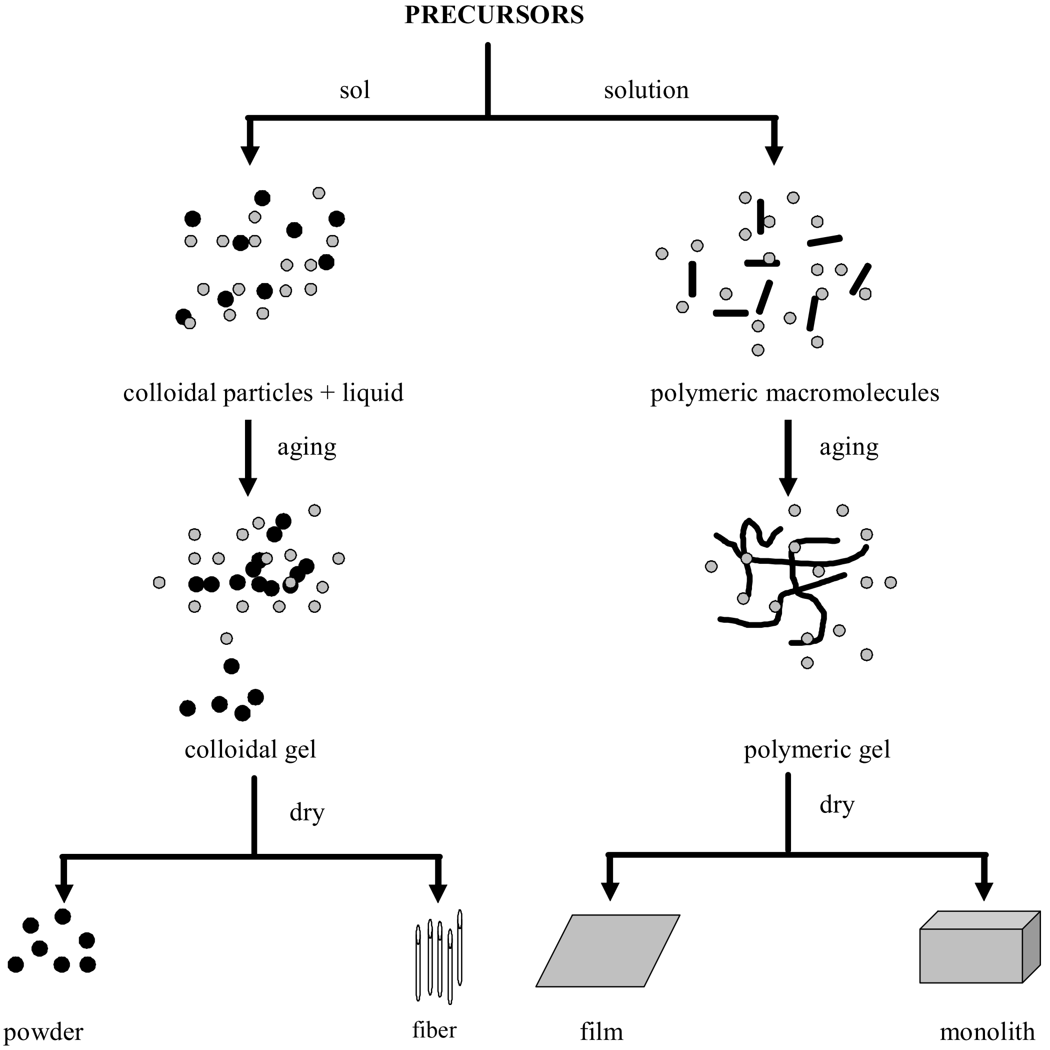

Figure 1. Generalized scheme of sol-gel synthesis.

6. It facilitates to form films of complex oxides and eases to control of composition and microstructure of the deposited films.

The sol-gel coating is almost exclusively applied for fabrication of transparent layers with a high degree of planarity and surface quality. The substrates that are used in this process have to withstand the required calcining and annealing temperatures due to the ZnO is formed through polycondensation at about 500 °C (Brinker & Schere, 1990).

STRUCTURAL PROPERTIES OF ZnO THIN FILM

The orientation of thin film is an important key that affects the final properties. The occurrence of preferred orientation can be explained by Morinaga and coworkers (Morinaga et al., 1997). A qualitative idea of the formation mechanism of preferentially oriented thin film could be suggested by considering the minimization of the surface free energy of each crystal plane and films usually grown to minimize the surface free energy; for example, ZnO thin films should be grown with a c-axis orientation according to the theoretical result of the surface free energy, the value of the surface free energy for ZnO (0001) plane or c-axis is minimum (0.099 eV). So, many researchers have studied the influence of deposition parameters on the structural properties of ZnO thin film.

The ZnO thin films have been crystallized at different temperatures when using the different complexing agents or stabilizers. The crystallization started from the temperature of 300 °C when using diethylenetriamine as complexing agent, and from 200 °C when using diethanolamine, monoethanolamine and acetylacetone as complexing agents. Moreover, only (002) plane grew rapidly from 400 °C when preparing from the solution of monoethanolamine and acetylacetone while the thin film from the diethylenetriamine homogeneously grew without preferential orientation (Nishio et al., 1996).

The orientation of ZnO thin film is also dependent on the nature of the solvent. The thin films which were prepared from ethanol solution showed no preferential orientation whereas changing the solution to 2-methoxyethanol resulted in a good preferential orientation of (002) plane perpendicular to the substrate. This preferential alignment could arise from the difference in boiling point and ability to form a complex with Zn^{2+} cations. 2-Methoxyethanol can more completely form complex with Zn^{2+} than ethanol. Ethanol is more volatile than 2-methoxyethanol (boiling point of ethanol = 78 °C, boiling point of 2-methoxyethanol = 125 °C) so its evaporation is easier leading to the formation of small agglomerated particles unable to develop a definite orientation.

Besides, the orientation of thin films is dependent on the concentration of precursor and molar ratio of complexing agent to precursor as well. The thin films made up from the concentrated solution yielded *c//n* orientation. On the contrary, the *a//n* orientation was only obtained when using the dilute solution as shown in Figure 2 (Znaidi et al., 2003).

Other parameters that influence on ZnO thin film are pre-heating and post- heating or annealing temperature for solvent vaporization and reagent decomposition. If pre-heating temperature was low (<300 °C), the (100), (002), and (101) diffraction peaks appeared and had a random preferential growth because the complete vaporization and thermal decomposition of precursor did not occur at this temperature but they occurred at post-heating temperature over 500 °C. In such a case, abrupt solvent vaporization and precursor decomposition occurred which might also disturb the unidirectional crystal growth. On the contrary, when the pre-heating temperature was higher (>300 °C), the films had more preferred (002) orientation as shown in Figure 3, because the structural relaxation of the gel film before crystallization more easily occurred at higher temperature (Lee et al., 2003).

The withdrawal speed of samples also acts on the occurrence of preferential orientation. The films had higher degree of orientation if the withdrawal speed was low as depicted in Figure 4 because the solvent and organic substances produce by thermal decomposition could evaporate more easily out of thinner films without disturbing the oriented crystal growth (Ohyama et al., 1997).

The orientation is also dependent on doping concentration that adds into solution, but this parameter does not act in all cases. Bandyopadhyay et al. (2002) had found that the thin film exhibited (100), (002), and (101) diffraction peaks whereas another researcher had discovered that the ZnO thin films had only (002) diffraction peak. In addition, peak intensity decreased with increasing doping concentration over 1 at. %, indicating that an increase in doping concentration deteriorated the crystallinity of films which might be due to the formations of stresses by the difference in size between zinc and dopant as well as the segregation of dopants in grain boundaries for high doping concentration. Furthermore, doping concentration plays important role on grain size. When the doping concentration increases the size of the grains began to decrease, the grains were more densely packed in highly doped films as well as the surface reveals lower porosity then become roughly constant. For example, the grain size of undoped ZnO was about 90 nm while it was about 40 nm for films with 1 at.% Al and remained almost the same for films with 2 at.% Al as shown in Figure 5 (Lee et al., 2003).

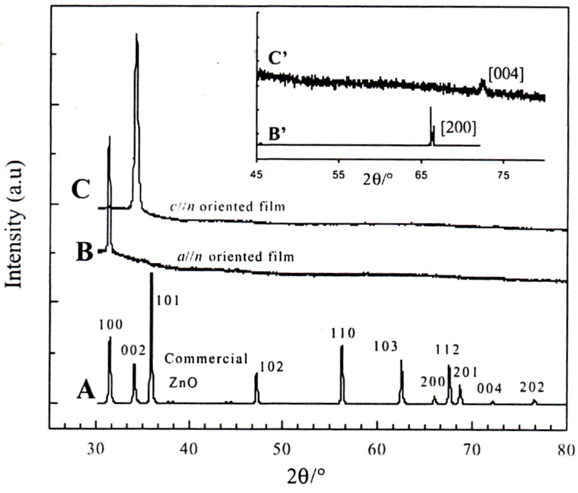

Figure 2. (A) XRD patterns of commercial zincite reference/ and ZnO oriented films, (B) *a//n* orientation, obtained from a 0.05 M solution, and (C) *c//n* orientation, obtained from a 0.75 M solution. Inset shows the zoom views of the B and C diffractograms in the 20-80° range (B' and C', respectively).

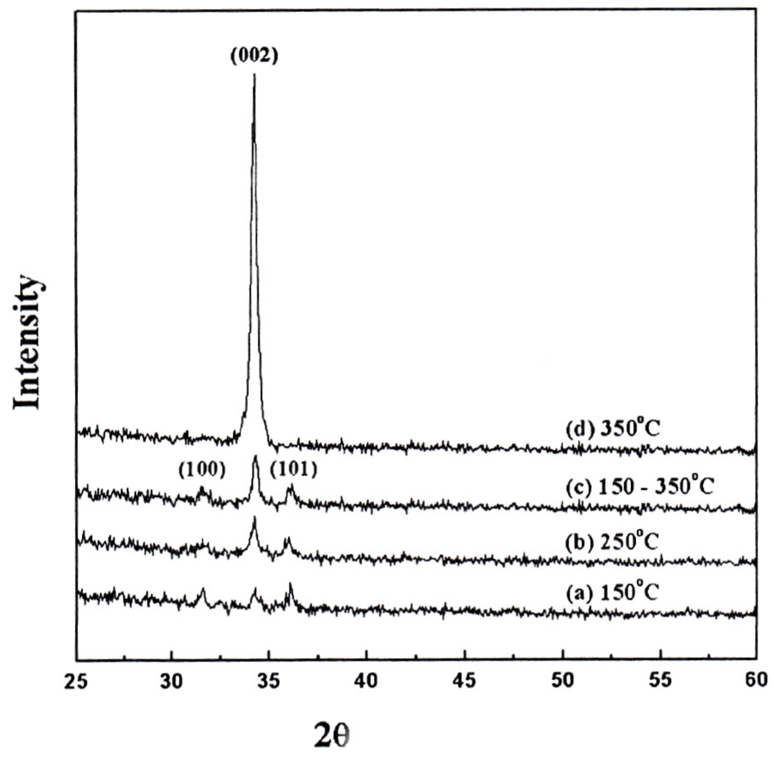

Figure 3. XRD patterns of ZnO films dried with different conditions and annealed at 600 °C for 1 h.

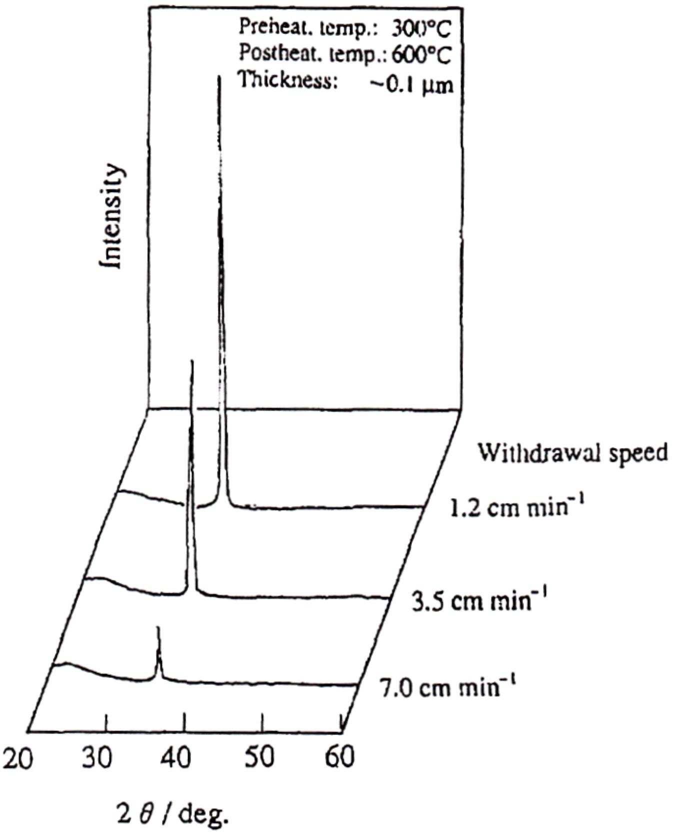

Figure 4. The XRD patterns of the ZnO films prepared by repeating the dip-coating at withdrawal speed of 1.2, 3.5 and 7.0 cm·min^{-1} and pre-heating at 300 °C and post-heating at 600 °C.

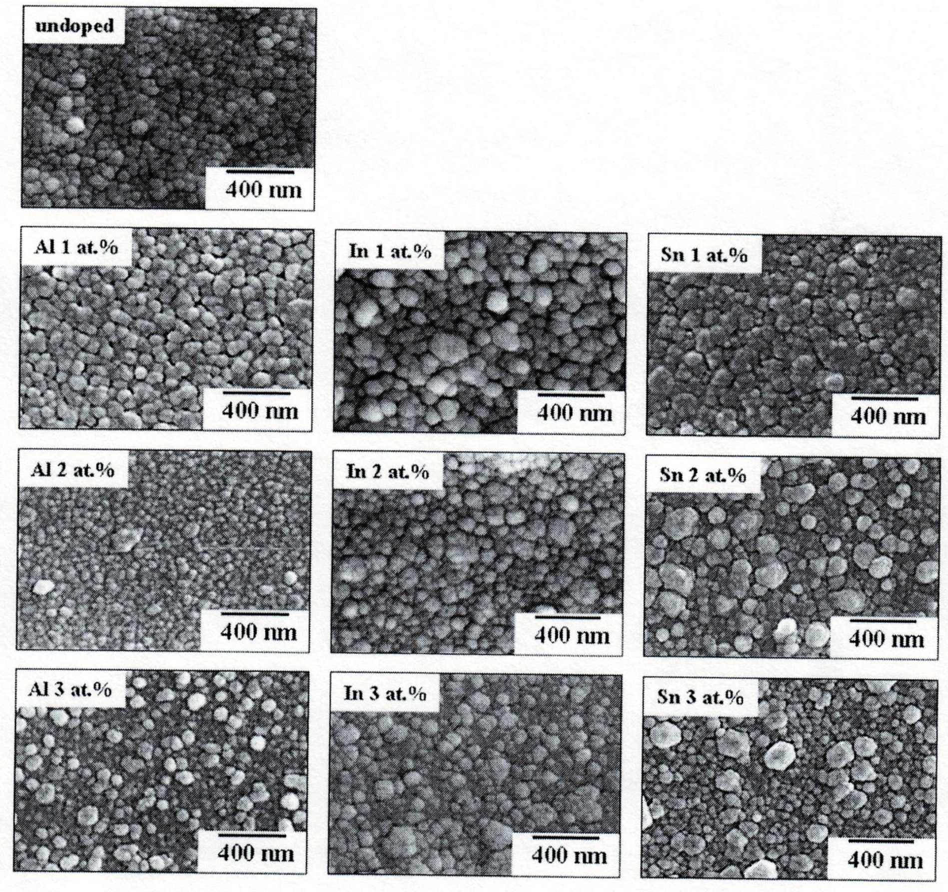

Figure 5. SEM images of undoped and doped ZnO thin films with various dopant contents.

ELECTRICAL PROPERTIES OF ZnO THIN FILM

The electrical conductivity of ZnO thin film is generated by defects such as zinc excess at the interstitial position and oxygen vacancies.

The orientation is one of the significant parameters that influence on electrical properties. It was found that the higher crystal orientation of the films perpendicular to the substrate performed lower resistivity, due to the shorter carrier path length in a c-plane and due to the reduction in the scattering of carriers at the grain boundaries and crystal defects. So, the apparent carrier mobility increased in this case (Musat et al., 2004).

It has also been reported that the electrical properties depend on the heat treatment temperatures. Natsume & Sakata (2000) had observed that the resistivity of ZnO films gradually decreased with the increasing annealing temperature from 23 °C to 525 °C with a minimum resistivity of 28.5 Ω·cm at 525 °C due to an improvement in the orientation of the films. However, they had also reported that the resistivity of ZnO films when annealing at higher temperature of 525 °C increased again. This might be due to the precursors are more completely decomposed and oxidiced, and then can form a better stoichiometry of ZnO films, therefore, the defects that can produce the donor levels decreased, affecting the decrease of carrier concentration.

Ohyama and coworkers (1998) had investigated the effect of pre-heating and post-heating treatment on resistivity of the films that contained 5 at. %Al and these films were prepared with a low substrate withdrawal speed (1.2 cm·min^{-1}). In the first case, the total heat treatment of films included a pre-heating of individual layer in the range of 200 °C to 450 °C in air, a post-heating of entire films at 600 °C in air and then a post-heating treatment at 600 °C in nitrogen, the resistivity value of 6.5 x 10^{-3} Ω·cm was achieved when using pre-heating temperature at 400 °C. Then, in the second case, the films were prepared with a maintaining pre-heating at 400 °C in air, a post-heating in the range of 500 °C to 700 °C in air, and then a post-heating treatment at 600 °C in nitrogen, the resistivity was achieved with a minimum value at 600 °C as in the first case.

An annealing with reducing atmosphere affected the decrease of resistivity, for example, the resistivity for H_2-annealed ZnO films gradually decreased from 500 °C to 550 °C, and then slightly increased up to temperature of 575 °C. The resistivity showed a minimum value of 0.09 Ω·cm at annealing temperature of 575 °C.

This resistivity value was approximately two orders of magnitude lower than the minimum resistivity (28.2 Ω·cm) of the film deposited at temperature of 525 °C. Thus the post-annealing in H_2 was effective for decreasing resistivity. The reactions in polycrystalline bulk ZnO were given by these relations (Natsume & Sakata, 2002).

$$\mathrm{ZnO} \Leftrightarrow \mathrm{Zn_i^{\cdot}} + e^- + \frac{1}{2}\mathrm{O_{2\,(g)}}$$

$$\mathrm{ZnO} \Leftrightarrow \mathrm{Zn_i^{\cdot\cdot}} + 2e^- + \frac{1}{2}\mathrm{O_{2\,(g)}}$$

The ZnO contains interstitial Zn atoms (Zn_i) due to presence of large voids and oxygen vacancies (V_o). So, the decrease of resistivity after annealing under hydrogen atmosphere might be due to the oxygen desorption from the surface, pores and grain boundaries, resulting in creation of vacant sites which acted as donor states.

Baik & Cha (1999) had studied the effect of dopant concentration on film resistivity. They found that the 0.5 at.%Al doped ZnO film which was annealed at 450 °C for 1 hour under vacuum or hydrogen environment showed the resistivity of 8×10^{-3} Ω·cm, whereas the undoped ZnO film showed the resistivity of 2×10^{-2} Ω·cm. Besides, other researchers had reported that the resistivity can be improved when using doping concentration between 1 and 2 at.%. For example, Jin-Hong L. and Byung-Ok P. (Lee & Park, 2003) had reported that the ZnO and 1 at. %Al doped ZnO films, which were annealed at 600 °C for 1 hour in air and then were annealed at 500 °C for 1 hour in nitrogen with 5% hydrogen, gave the resistivity of 10^{-1} Ω·cm and 10^{-2} Ω·cm, respectively. This can be explained by an increase in carrier concentration. Such behavior was expected as a result of substitutional doping of Al at the Zn site creating one extra free carrier in the process. Generally, the segregation of aluminium (as Al_2O_3) at the grain boundaries had been avoided and an effective substitution of the dopant (Al) atoms in Zn sites of ZnO structure took place according to the following equation (Musat et al., 2004).

$$\mathrm{Al_2O_3} \longrightarrow 2\mathrm{Al_{Zn}^{\cdot}} + 2\mathrm{O_O} + \frac{1}{2}\mathrm{O_2} + 2e^-$$

As the doping content was increased, more dopant atoms occupied lattice sites of zinc atoms, resulting in more free charge carriers. However, after a certain level of doping, no more zinc sites can be occupied by dopant atoms because of the limited solubility of aluminium in the ZnO crystallites. According to the smaller ionic radius of aluminium ($r_{Al^{3+}}$ = 0.054 nm) comparing with ionic radius of zinc ($r_{Zn^{2+}}$ = 0.074 nm), the excess aluminium might occupy interstitial positions leading to distortion of the crystal structure or aluminium atoms might also segregate at grain boundaries in the form of Al_2O_3 which increased the grain boundary barrier (Baik & Cha, 1999; Lee & Park, 2003; Musat et al., 2004).

OPTICAL PROPERTIES OF ZnO THIN FILM

Optical band gap measurements on ZnO thin films performed in the range from 3.31 to 3.44 eV and ZnO crystal gave an optical band gap equal to 3.3 eV. The band gap difference of the film and crystal is caused by the existence of grain boundaries and imperfections in polycrystalline thin film. Moreover, atomic structure at grain boundary is different from atomic structure in the grain which leads to larger free carrier concentrations and presence of potential barriers at boundaries. Therefore, the electric field is formed. This leads to the increase of the band gap (Bao et al., 1998).

Optical properties strongly depend on surface morphology of ZnO thin films. The transmittance increased after heat treatment at 600 °C in air and at 500 °C under nitrogen with 5% hydrogen might be due to an increase of optical scattering caused by the densification of grains followed by grain growth and reduction of grain boundary density as depicted in Figure 6 (Lee et al., 2003).

The optical properties are also dependent on annealing temperature. Generally, oxygen is chemisorbed on ZnO surface and in pores as O_2^- by accepting an electron from occupied conduction band states. Therefore, oxygen desorbs as increase in annealing temperature causing the shift of absorption edge due to increase in carrier concentration.

The doping concentration influences the optical properties as well. The thin films with different doping concentrations are highly transparent in visible region with a transmission of more than 80% and the sharp absorption spectra were observed at around a cut-off wavelength which indicated that ZnO had direct energy band gap. The absorption edge of Al doped ZnO thin films shifted to a shorter wavelength (blue shift) compared with the undoped ZnO thin film. This absorption edge shift was caused by the fact that an increase in the carrier concentration gave rise to an increase in energy band gap (Baik & Cha, 1999; Valle et al., 2004).

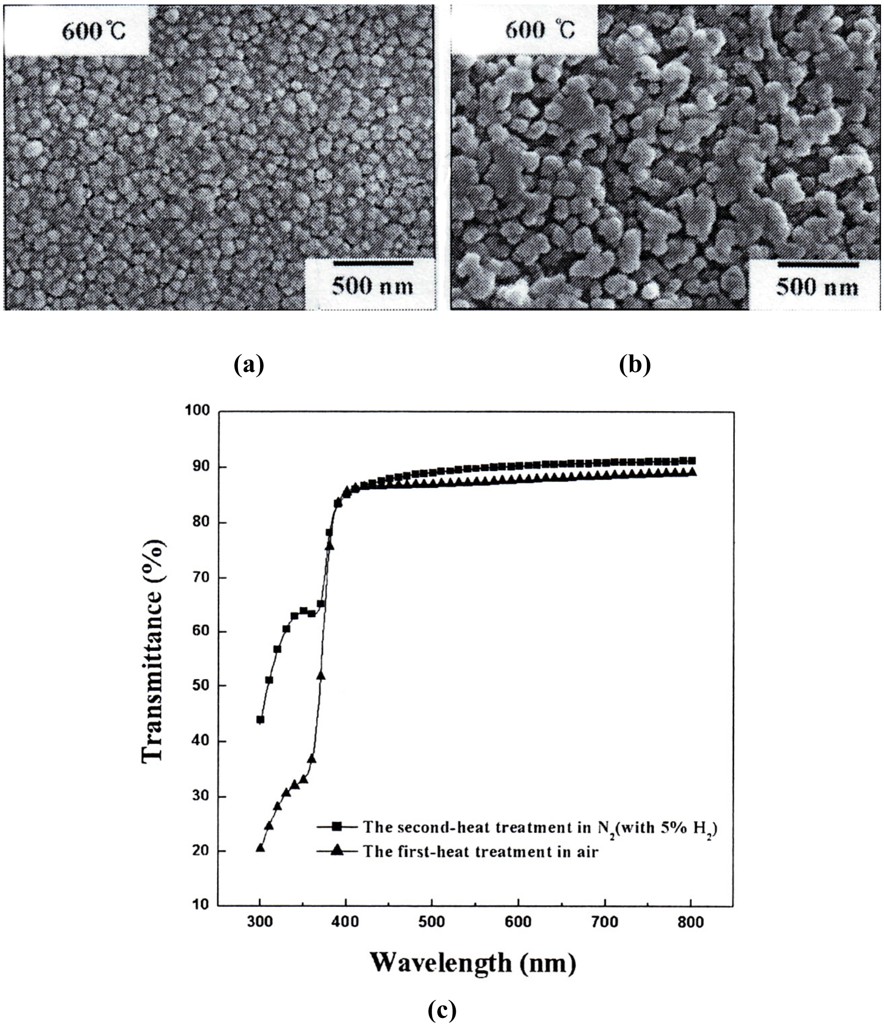

Figure 6. (a) SEM images of ZnO films dried at 350 °C with first-heat treatment at 600 °C, (b) ZnO films dried at 350 °C with first-heat treatment at 600 °C and second-heat treatment in N_2 (with 5%H_2) and (c) optical transmittance spectra of the films in (a) and (b).

CONCLUSION

This review showed that the orientation and grain size of ZnO thin films prepared by sol-gel method depending on the concentration of zinc salt, complexing agent or stabilizer and dopant as well as heat treatment temperature. The ZnO thin films which had a smaller grain size and good preferential orientation performed better optical and electrical properties.

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