

Colloidal dispersion of nano-scale ZnO powders using amphibious and anionic polyelectrolytes

Kuo-Liang Ying, Tsung-Eong Hsieh^{*}, Yi-Feng Hsieh¹

Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta-Hseuh Road, Hsinchu 30010, Taiwan, ROC

Received 18 September 2006; received in revised form 6 August 2007; accepted 30 May 2008

Available online 22 July 2008

Abstract

This article describes the dispersion of aqueous suspensions containing nano-scale ZnO powder by utilizing a hybrid of chemical dispersant and mechanical mixing/grinding process. The chemical dispersants included anionic or amphibious polyelectrolytes, *i.e.*, sodium salt of polymethylacrylic acid (PMAA-Na) or polyacrylamide/(α -N, N-dimethyl-N-acryloyloxyethyl) ammonium ethanate (PDAAE). The optimum critical concentrations for each dispersants to achieve the lowest viscosity, smallest final sediment volume and particle size (d_{50}) for the nano-ZnO suspensions, 3 wt.% for PMAA-Na and 5 wt.% for PDAAE, were identified. The finely dispersed nano-ZnO powders were transferred to prepare sputtering target. The root-mean-square roughness (R_{RMS}) of thin films deposited by utilizing such a target was found to be 2.05 nm, which was lower than the R_{RMS} of the film (≈ 27.57 nm) deposited by using a commercial ZnO target comprised of micro-scale granules.

© 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: ZnO; Nano-scale dispersion; Polyelectrolytes; Nano-ZnO target

1. Introduction

Zinc oxide (ZnO) has been widely studied over the past two decades since it is a rather promising material for optical, electrical, catalytic and piezoelectric applications, *e.g.*, solar cells, ultra-violet light-emitting diodes (UV-LED), optical waveguides, varistors, gas sensors, surface acoustic wave (SAW) devices, transparent conducting electrodes and field emission devices. At present, indium tin oxide (ITO) is the most common transparent conducting material for flat panel displays (FPDs) [1]. However, recent studies reported that ZnO is one of alternatives with great potentials for similar application. The transparent conducting electrodes are in general prepared by sputtering method and, to obtain the thin-film layer with good surface flatness and electrical properties, a sputtering target with high packing density and uniform microstructure is essential [2]. Poor flatness is undesired since the spikes on the surface of electrode may cause the discharge and result the bright spot defects on the FPDs. Specific deposition method

such as negative sputter ion beam (NSIB) was carried out to improve the surface flatness of transparent conducting electrode [3–5]; however, it was a relatively expensive process. This work intends to improve the flatness of electrodes by utilizing the ZnO target prepared by the finely dispersed nano-ZnO powders.

Ceramic sputtering targets are usually synthesized *via* sintering process. Before the thermal treatment, the preparation of powders with uniform particle size and slurries with satisfactory dispersion are essential. For the nano-scale powders, dispersion is a must since they exhibit large van der Waals attractive force and specific surface area (SSA) [6]. In conventional ways, organic solvents are used to disperse the inorganic powders. At present, the preparation of aqueous-based suspensions becomes more attractive due to safety, economic and environmental reasons [7]. Chemical dispersants, acrylic acid-based polyelectrolytes are often used for the dispersion of ceramic powders [8–10]. For example (poly-methacrylic acid) (PMAA-NH₄) and polyacrylic acid (PAA) has been applied to disperse alumina (Al₂O₃) [11–13], barium titanate (BaTiO₃) [14–16] and silicon nitride (SiN_x) [17–20] suspensions. Amphibious polyelectrolytes such as PDAAE were also applied to disperse the BaTiO₃ suspensions [21,22]. Previous study found that a sole chemical dispersant is

^{*} Corresponding author. Tel.: +886 3 5712121x55306; fax: +886 3 5724727.

E-mail address: tehsieh@cc.nctu.edu.tw (T.-E. Hsieh).

¹ Currently at Taiwan Semiconductor Manufacturing Co. (TSMC), Taiwan, ROC.

insufficient and the incorporation of mechanical mixing is required to achieve a full nano-scale dispersion [6].

In this work, dispersion of nano-scale ZnO powder in aqueous suspensions by using PDAAE or PMAA-Na incorporating with a mechanical mixing/grinding process was investigated. The optimum concentration of dispersants was concluded from the study and the nano-ZnO target was prepared by utilizing the finely dispersed powders. The surface roughness of thin films deposited by using the nano-ZnO and commercial micro-ZnO targets were compared and the relationship between granular structure of sputtering target and deposited film was discussed.

2. Experimental

2.1. Raw materials

The ZnO powder (Seedchem, Australia, purity = 99.5%) with a specific surface area of 10.02 m²/g and an average particle size of 70 nm was utilized in this work. The PDAAE ($M_w = 1.0 \times 10^4$) was prepared by using acrylamide (AAM) and (α -N,N-dimethyl-N-acryloyloxyethyl) ammonium ethanate (DAAE) via free-radical polymerization process and preparation procedures for PDAAE could be found elsewhere [21,22]. The other type of dispersant, PMAA-Na with $M_w = 1.0 \times 10^4$ was supplied by Echo Chemicals. Fig. 1 shows the chemical structures of PDAAE and PMAA-Na dispersants.

2.2. Sample preparation and property characterizations

2.2.1. Preparations of ZnO suspensions

The as-received ZnO powders were first rinsed in de-ionized water and then dried over night at about 80 °C before colloidal preparation. Aqueous slurries of 100 g in weight containing either 15 wt.% or 60 wt.% ZnO powder were prepared. The pH values of slurries were measured accordingly and found about equal to 9. In the meantime, the chemical dispersants were dissolved in de-ionized water and the pH value of solutions were adjusted to 9 by adding appropriate amounts of NaOH_(aq). The purpose of this procedure is to ensure the complete dissociation of chemical dispersants [21,22]. The suspensions containing various amounts of chemical dispersants in the range of 0–7 wt.% relative to the mass of dry ZnO powder were

then prepared by mixing the ZnO slurry and dispersant solution together. Afterward, all the suspensions were sent to a laboratory mill (MiniZeta 03, NETZSCH-Feinmahltechnik GmbH) for mechanical mixing/grinding. After grinding, a small amount of slurry was taken out for subsequent property characterizations. The pH values of suspensions subjected to mechanical mixing/grinding were also checked and a value about 9 was observed. This indicates that there is no dissolution of ions during mechanical mixing/grinding of ZnO slurries performed in this work.

2.2.2. Viscosity

After the mechanical mixing/grinding, the viscosities of 60 wt.% ZnO suspensions containing various amounts of PMAA-Na or PDAAE were analyzed by using a rheometer (DV-II, Brookfield Engineering Lab.) in order to determine the degree of particle coagulation in suspensions. Rheological characterizations were performed at room temperature with concentric cylinder measurement geometry. The suspensions were subjected to a high shear rate of 100 s⁻¹ to break up any initial network structure.

2.2.3. Particle size distribution

A small amount of 15 wt.% ZnO suspensions with or without chemical dispersants were taken out after mechanical mixing/grinding process. The samples were transferred to a particle size analyzer (Malvern Mastersizer 2000) for the measurement of particle size distributions of ZnO powders.

2.2.4. Zeta potential

Aqueous suspensions of 15 wt.% ZnO with or without chemical dispersants subjected to mechanical grinding/mixed were centrifuged a speed of 3000 rpm for 30 min to obtain the supernatants. A small amount of supernatant was taken out from each of the samples and a zeta meter (PEN KEN Inc. 501) was adopted to measure the zeta potential of the remaining powders in the supernatant.

2.2.5. Adsorption of dispersants

Aqueous suspensions containing 15 wt.% ZnO powder and 0–7 wt.% PDAAE or PMAA-Na dispersant subjected to mechanical mixing/grinding were prepared (pH 9). The adsorption isotherm of dispersant is determined as follows. The suspensions were first centrifuged at a speed 6000 rpm for 30 min to obtain supernatants. The dispersant concentration in the supernatant was then analyzed by potentiometric titration method [9,22]. The amount of dispersant adsorbed on the ZnO particles was determined in terms of the difference of dispersant concentrations in aqueous suspension and in the supernatant. The plot of dispersant amount adsorbed on the ZnO versus the initial dispersant concentration was constructed so as to explore the adsorption behaviors of chemical dispersants.

2.2.6. ZnO target preparation and surface roughness measurement

The previously prepared nano-ZnO powders were first pressed into disks about 2 in. in diameter and 5 mm in

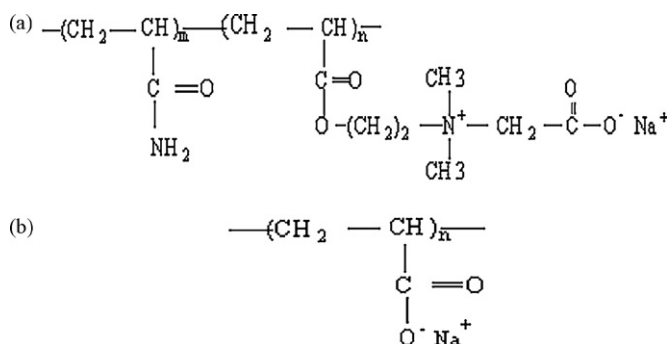


Fig. 1. Chemical structures of (a) PDAAE and (b) PMAA-Na polymers.

thickness and then isostatically pressed at the pressure of 11 kpsi. The ZnO disks were prepared by a two-step process: hot pressing at 700 °C for 8 h followed by isothermally soaking at 700 °C for 16 h. The thin films were deposited on glass substrates by using a self-designed sputtering system by utilizing either nano-ZnO or commercial ZnO target. The surface morphology of target samples was characterized by scanning electron microscopy (SEM, JSM-6500F, JEOL). Roughness of thin films was evaluated by an atomic force microscope (AFM, Nano Scope Dimension 3100, Digital Instruments).

3. Experimental results

3.1. Rheological behaviors

Fig. 2 presents the viscosities of 60 wt.% ZnO suspensions as a function of the concentration of PMAA-Na and PDAAE at the value of pH 9. Regardless of the dispersant types, the viscosities first decrease with the increase of dispersant contents, then increase with further increase of dispersant contents. Since high viscosity values indicate the occurrence of flocculation in the suspensions, Fig. 2 clearly reveals that there exists an optimum content for each type of dispersants that must be added to secure satisfactory stabilization in suspensions. The optimum amount of the dispersant, which gave the lowest viscosity, was 3 wt.% for PMAA-Na and 5 wt.% for PDAAE, respectively. The minimum viscosities corresponding to these optimum dispersant concentrations were 6 Pa s for PMAA-Na and 11 Pa s for PDAAE, respectively. Fig. 2 shows that both the addition of PMAA-Na or PDAAE may effectively reduce the viscosity of suspensions and, for PMAA-Na, it exhibits the sharper decline of the viscosity of suspensions and the amount of dispersant to achieve the minimum viscosity is less than that of PDAAE. Furthermore, the minimum viscosity of the suspensions achieved by PMAA-Na is lower than that by PDAAE.

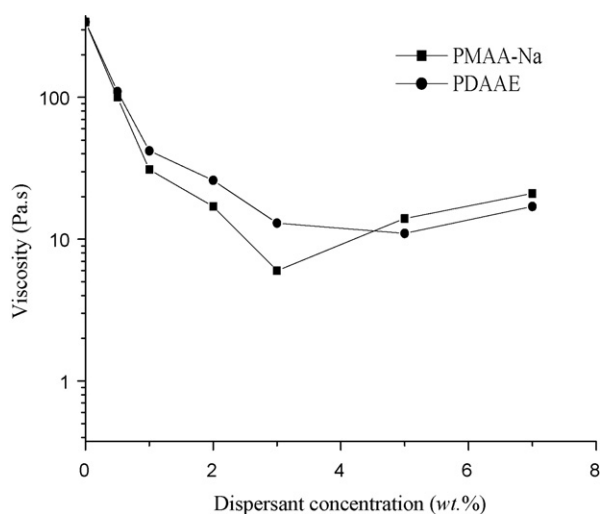


Fig. 2. Effect of dispersant concentration on the viscosity of 60 wt.% ZnO suspensions at pH 9.

3.2. Particle size distribution

Fig. 3 shows the plot of mean particle size (d_{50}) of ZnO powders in 15 wt.% suspensions versus the dispersant concentration. For the suspensions without dispersants, the d_{50} is about 0.3 μm . It shifts to a smaller value when dispersants are added. For the PDAAE suspension, the minimum d_{50} of 62 nm occurs at about 5 wt.% of dispersant concentration. For the PMAA-Na suspension, the minimum d_{50} about 60 nm occurs at about 3 wt.% dispersant concentration. The suspensions containing PDAAE require a larger amount of dispersants and show a slightly larger minimum d_{50} than the suspensions containing PMAA-Na.

Fig. 4 illustrates the particle size distributions of 15 wt.% ZnO suspensions containing 3 wt.% PMAA-Na, 5 wt.% PDAAE and none of chemical dispersant subjected to mechanical mixing/grinding. The distribution profiles corresponding to the suspensions containing chemical dispersants are narrow and sharp in shape with the sizes ranging from about 35 to 90 nm. Furthermore, the mean particle sizes deduced from the peaks of profiles are in good coincidence with the d_{50} values presented in Fig. 3. As to the ZnO suspension free of chemical dispersant, it possesses a broad size distribution from 0.1 to 1 μm with peak value at about 240 nm. The narrow and sharp shapes of size distribution profiles evidence the highly uniform particle sizes in the ZnO suspensions containing chemical dispersants and the success of dispersion process combining chemical dispersant and mechanical mixing/grinding presented in this work.

3.3. Zeta potentials

Fig. 5 shows the zeta potentials of dispersant-free 15 wt.% ZnO suspensions as a function of pH values. At low pH values, the zeta potential, or the surface charge, of ZnO particles is positive. With the increase of pH values, the surface charge decreases and at high pH values, the zeta potential becomes

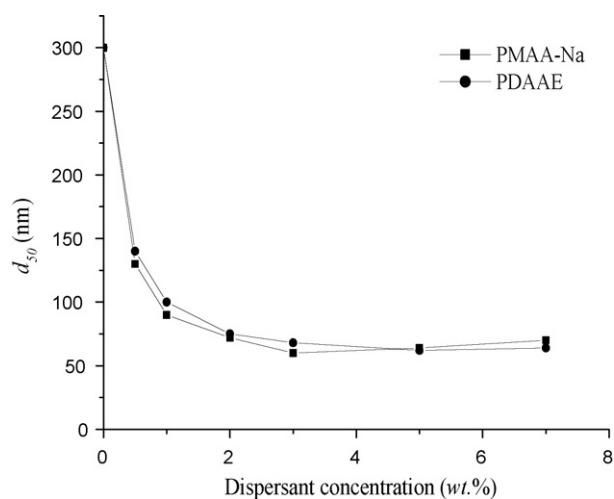


Fig. 3. Effect of dispersant concentration on the mean particle size (d_{50}) of ZnO powders in 15 wt.% suspensions.

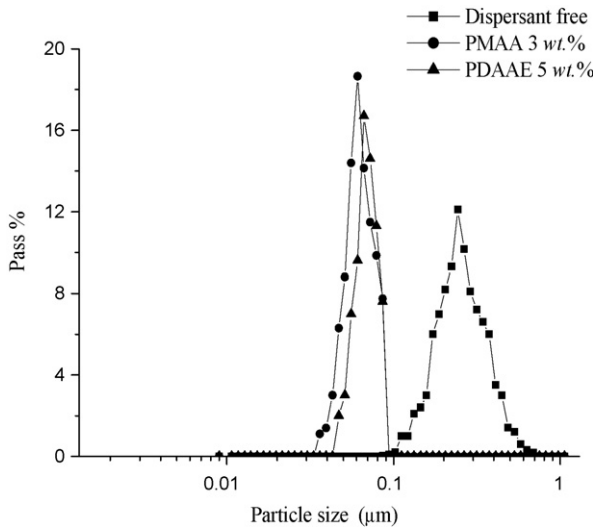


Fig. 4. Particle size distribution of ZnO powders in the slurries containing 3 wt.% PMAA-Na, 5 wt.% PDAAE and free of chemical dispersant subjected to mechanical mixing/grinding process.

negative. The isoelectric point or the zero net surface charge occurs at about pH 8.6.

Fig. 6 shows the effects of dispersant content on the zeta potential of 15 wt.% ZnO suspensions at pH 9. The zeta potential of suspensions free of dispersant is -2 mV. With the introduction of dispersant in the suspensions, the value becomes more and more negative and then gradually reaches a plateau value. For suspensions containing PMAA-Na, the zeta potential declines faster and the plateau value is more negative in comparison with those containing PDAAE.

3.4. Surface roughness of deposited films

Fig. 7(a and b), respectively shows the SEM micrographs of nano-ZnO target before and after hot-pressing treatment. It can be seen that the grain sizes of ZnO powders increase to about 200 nm after hot pressing and the relative density is about 93% as

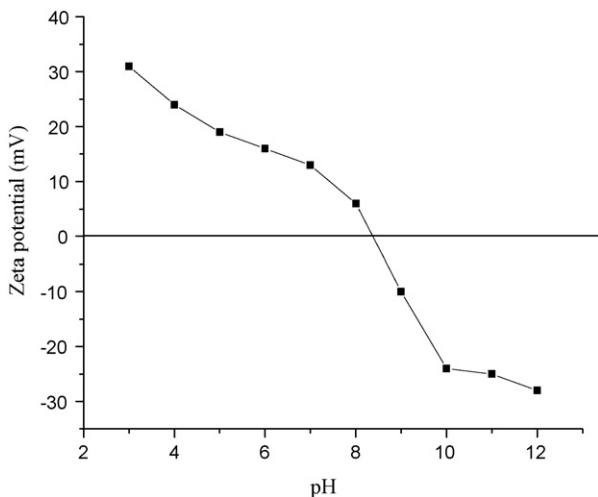


Fig. 5. Zeta potentials of ZnO particles in dispersant-free 15 wt.% ZnO suspensions as a function of pH values.

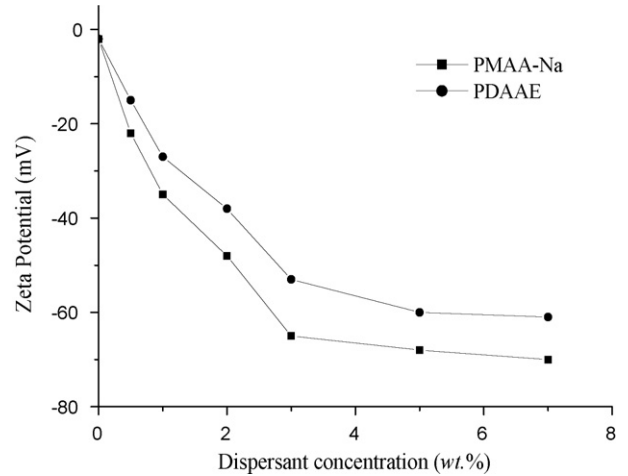


Fig. 6. The effect of dispersant content on the zeta potential of 15 wt.% ZnO suspensions at pH 9.

revealed by the density measurement. The AFM morphologies of as-deposited films prepared by using the commercial and nano-ZnO targets are presented in Fig. 8(a and b), respectively. Typical roughness plots for these two types of thin-film samples are given in Fig. 9(a and b). In terms of AFM characterizations presented in

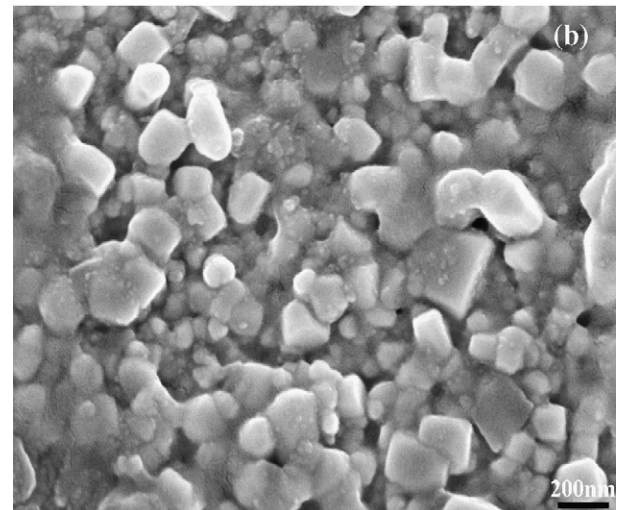
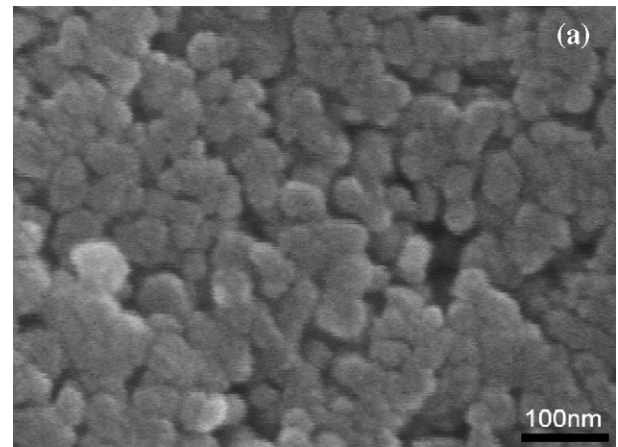


Fig. 7. The microstructure of nano-ZnO target (a) before and (b) after hot-press treatment.

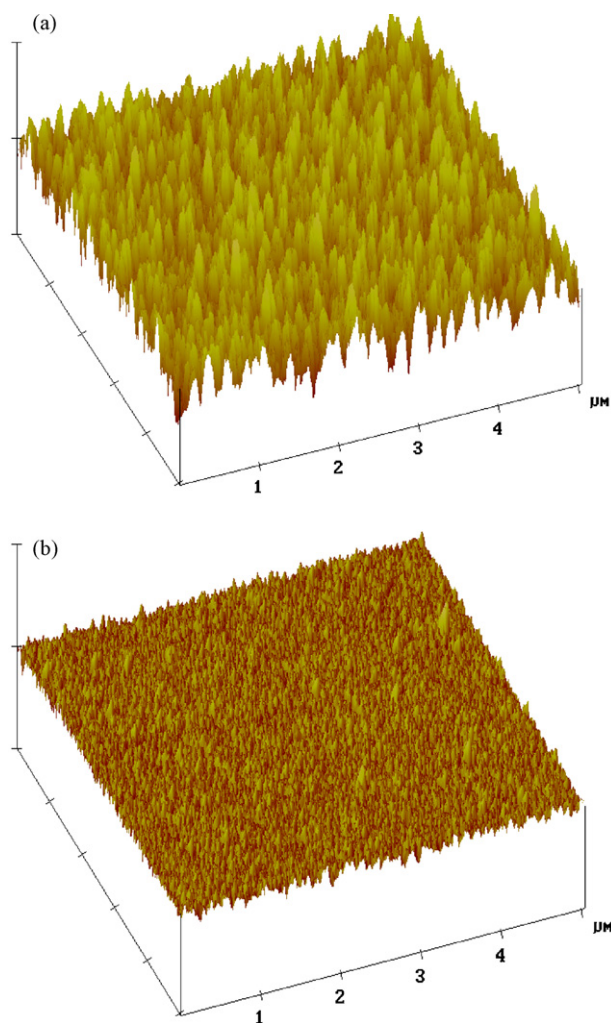


Fig. 8. The AFM surface morphology of the as-deposited films prepared by (a) commercial micro-ZnO and (b) nano-ZnO targets.

Figs. 8 and 9, the $R_{\text{RMS}} = 34.36$ nm and mean roughness = 27.57 nm for the films deposited by using the commercial ZnO target while for the film prepared by using nano-ZnO target, the $R_{\text{RMS}} = 2.05$ nm and mean roughness = 1.93 nm.

4. Discussion

Experimental results presented above indicated that both PMAA-Na and PDAAE are capable of stabilizing the nano-scale ZnO suspensions. However, more amount of PDAAE was required to achieve the minimum viscosity and the minimum viscosity of the suspension achieved by PMAA-Na was lower than that by PDAAE. This could be explained by the difference of dispersion behaviors provided by the dispersants. As shown in Fig. 1, PMAA-Na is an anionic polyelectrolyte causing mainly the electrostatic repulsions in suspensions when adsorbed on ZnO particles. PDAAE also causes electrostatic repulsions; however, such an effect is less in comparison with PMAA-Na because PDAAE is an amphibious polyelectrolyte. It was speculated that PDAAE generates more steric effects because its molecules contain longer side chains.

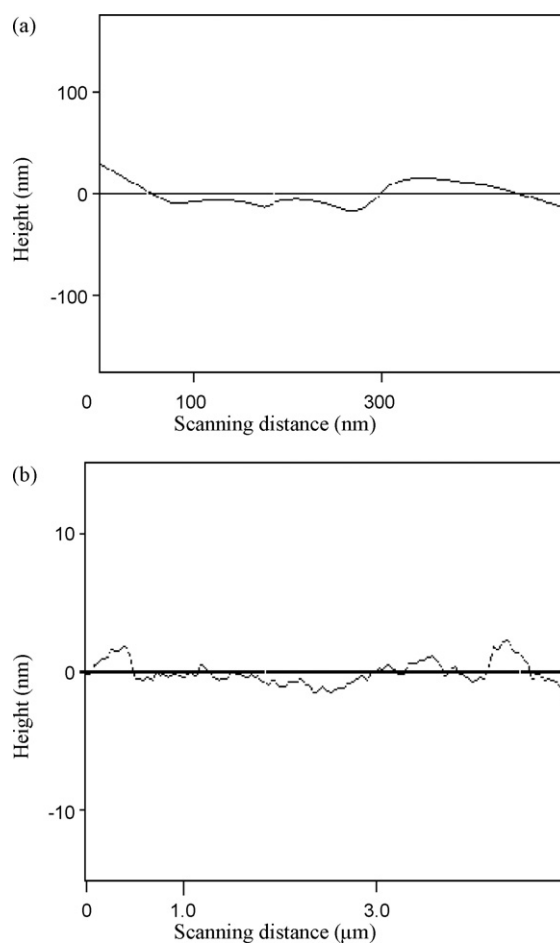


Fig. 9. The roughness plot of as-deposited films prepared by (a) commercial micro-ZnO and (b) nano-ZnO targets.

It is known that the dispersion or stabilization of aqueous suspensions *via* the addition of polyelectrolytes consequently reduces the viscosity. Nevertheless, too low viscosity of suspensions induces fast sedimentation. The low-viscosity suspension is inadequate for subsequent green tape preparation since it implies poor sintering density and properties [17]. It was hence concluded that PDAAE is a more appropriate chemical dispersant for nano-scale ZnO suspensions.

As shown in Fig. 1, the PMAA-Na molecules contain a functional group $-\text{COO}^- \text{Na}^+$. When the PMAA-Na and PDAAE are dissolved in aqueous solutions, the functional group dissociates into $-\text{COO}^-$. The fraction dissociated or the percentage of the number of $-\text{COO}^-$ to the total number of functional groups is affected by the pH values of the solution. The PMAA-Na starts to dissociate at $\text{pH} > 2$ and the fraction dissociated increases with the increase of pH values. At $\text{pH} > 8$, PMAA-Na completely dissociates and become effectively negatively charged [20].

As shown in Fig. 1, the PDAAE copolymer synthesized by the reaction of AAM and DAAE monomers contains not only the anionic functional groups ($-\text{COO}^-$) similar to PMAA-Na, but also the cationic functional groups ($-\text{N}^+$). Though the dissociation behavior of PDAAE molecules is similar to that of PMAA-Na molecules (for anionic functional groups ($-\text{COO}^-$))

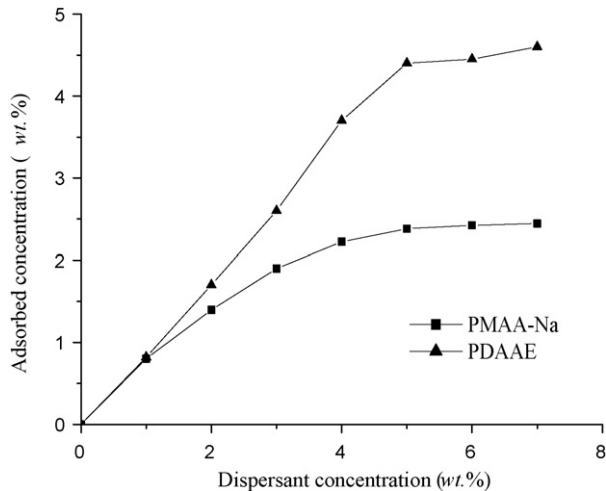


Fig. 10. The amount of dispersants adsorbed on ZnO particles as a function of the initial dispersant concentration at pH 9.

[20,21], their adsorptive behaviors on ZnO surface are distinct. The PDAAE molecules contain cationic functional groups ($-N^+R_3$), which favor themselves to be adsorbed on negative charge of nano-ZnO surface. As to PMAA-Na, it adsorbed on ZnO surface by weak van der Waals force [21].

Fig. 10 shows the concentration of the dispersants adsorbed on ZnO particles as a function of the dispersant concentration at pH 9. In general, the adsorbed amount increases quickly with the increase of dispersant concentration and then reaches a plateau value. The plateau value, or the critical value, accounts for the amount of dispersant required for the coverage of the particle surface. The critical value for PMAA-Na is about 3 wt.% (deduced from the viscosity test), and the adsorbed concentration is about 2.4 wt.%. As to the PDAAE, it possesses larger critical value and the adsorbed concentration, which are about 5 wt.% and 4.5 wt.%, respectively.

Comparing the rheological and the adsorption isotherm for PMAA-Na and PDAAE, it can be seen that the concentration of dispersant corresponding to the lowest viscosity of nano-ZnO suspensions also implies the situation where virtually all the dispersants are adsorbed on ZnO and there is a negligible amount of free dispersant remaining in the continuous phase. When the concentration of dispersant exceeds the optimum amount, the excessive dispersants may act as the free electrolytes in suspension. This would generate excessive ions and raise the ionic intensity in the suspensions. Compression of electro double layer thus occurs; it consequently disturbs the electrostatic forces in the system and hence increases the viscosity of suspension [9]. The good consistence observed in rheological and adsorption isotherm measurements suggests a monolayer of the dispersants adsorbed onto the nano-scale ZnO particles. Such an adsorption behavior provides the highest stability of suspensions at the experimental conditions adopted in this study.

The differences of critical values and the adsorbed amounts of the dispersants are also attributed to difference of chemical structures. At pH 9, PMAA-Na is completely dissociated and becomes negatively charged. Therefore, it is difficult for PMAA-Na molecules to be adsorbed on the negative-charged

ZnO surface. On the other hand, PDAAE becomes amphibious in a basic solution. The molecules contain cationic functional groups ($-N^+$), which favor themselves to be adsorbed on the ZnO surface. Accordingly, the adsorbed concentration of PDAAE (about 4.5 wt.%) in ZnO suspensions is larger than that of PMAA-Na (about 2.4 wt.%). Previous viscosity measurement indicated that addition of PMMA-Na provides a more successful dispersion of nano-scale ZnO in suspensions. Although, the adsorption of PMAA-Na on nano-scale ZnO was small than that of PDAAE, PMAA-Na was an anionic dispersant that could offer more electrical force than PDAAE on nano-ZnO particle surface.

The AFM characterizations presented in Figs. 8 and 9 reveal that the film sample deposited by using nano-ZnO target possesses a relatively small surface roughness value in comparison with the film prepared based on commercial ZnO target. Loren et al. [5] reported the film surface roughness increases with the increasing sizes of grains. Hence, when the size of sputtered granules leaving the target surface is large, the deposited film is speculated to have a rough surface due to the coarse grain structure. As presented in Fig. 7(b), the target prepared by using the nano-ZnO powders comprises of a fine granular microstructure of sizes ≈ 200 nm. During sputtering, relatively small ZnO granules bombarded away from the target could thus be expected. This results in a fine grain structure and implies a smooth surface of the deposited film. Above AFM and SEM results indicate that there is a correlation between microstructures of sputter target and deposited films. It is speculated that utilization of the nano-ZnO powders for target preparation may effectively improves the surface roughness of the deposited films by providing a fine microstructure. Hence, if applied to the fabrication such as transparent conducting electrodes, the FPD screen defects related to electrodes may be effectively suppressed.

5. Conclusions

Amphibious and anionic water-soluble copolymer, PDAAE and PMAA-Na, are utilized as a dispersing agent in combination of mechanical mixing/grinding for nano-ZnO aqueous suspensions. The experimental results are summarized as follows:

- (1) As indicated by viscosity measurement, both PMAA-Na and PDAAE showed good dispersion capability of nano-ZnO powders. Addition of PMAA-Na decreased the viscosity to a lower value since, as evidenced by the zeta potential measurements, such an anionic dispersant could offer more electrical force when adsorbed on the nano-ZnO surface.
- (2) Though electrostatic effects were comparatively less in comparison with PMAA-Na, PDAAE was in fact better to stabilize the nano-ZnO suspensions since its amphibious polyelectrolyte feature enables more dispersant absorption. Further, the longer side chain molecule structure of PDAAE provided more steric hindrance that benefited the suspension stabilization.

(3) AFM analysis revealed a lower surface roughness of ZnO film deposited by using the target prepared by using the finely dispersed nano-ZnO powders. This evidenced the correlation of grain microstructure of sputter target and deposited film. When applied to the fabrication of transparent conducting electrodes, utilization of fine granular sputter target might thus suppress the spike formation on electrode surface and consequently reduce the screen defects of FPDs.

Acknowledgements

This work was supported by the National Science Council (NSC) of the Republic of China under the Contract No. NSC93-2216-E-009-008. The hot-pressing process and part of SEM characterizations supported by Prof. Dennis C. Hsu's research group at Department of Materials Science and Engineering, National United University, is also deeply acknowledged.

References

- [1] E.V. Lavrov, *Physica B* 31 (2003) 195.
- [2] Y.C. Kang, S.B. Park, *Mater. Lett.* 40 (1999) 129.
- [3] M.H. Sohn, D. Kim, S.J. Kim, N.W. Paik, *J. Vac. Sci. Technol. A* 21 (2003) 1347.
- [4] D. Kim, *Opt. Mater.* 24 (2003) 471.
- [5] W. Loren, H. Rieth, P. Holloway, *J. Vac. Sci. Technol. A* 22 (2004) 20.
- [6] K.L. Ying, T.-E. Hsieh, *J. Appl. Polym. Sci.* 106 (2007) 1550.
- [7] M.C. Blanco-Lopez, B. Rand, F.L. Riley, *J. Eur. Ceram. Soc.* 17 (1997) 281.
- [8] A.W.M. de Laat, W.P.T. Derks, *Colloids Surf. A: Physicochem. Eng. Aspects* 71 (1993) 147.
- [9] J.H. Jean, H.R. Wang, *J. Am. Ceram. Soc.* 81 (1998) 1589.
- [10] J. Cesarano III, I.A. Aksay, A. Blier, *J. Am. Ceram. Soc.* 71 (1988) 250.
- [11] J. Cesarano III, I.A. Aksay, *J. Am. Ceram. Soc.* 71 (1988) 1062.
- [12] G. Bertrand, C. Filiatre, H. Mahdjoub, A. Foissy, C. Codde, *J. Eur. Ceram. Soc.* 23 (2003) 263.
- [13] A. Tsetsekou, C. Agraftotis, A. Miliadis, *J. Eur. Ceram. Soc.* 21 (2001) 363.
- [14] Z.C. Chen, T.A. Ring, J. Lemaitre, *J. Am. Ceram. Soc.* 75 (1992) 3201.
- [15] D.H. Napper, *Polymeric Stabilization of Colloidal Dispersions*, Academic Press, New York, 1983.
- [16] A.W.M. de Laat, G.L.T. Van den Heuvel, *Colloids Surf. A: Physicochem. Eng. Aspect* 98 (1995) 53.
- [17] C.J. Shih, H.M. Hon, *Mater. Chem. Phys.* 57 (1998) 125.
- [18] C.J. Shih, B.H. Lung, M.H. Hon, *Mater. Chem. Phys.* 60 (1999) 150.
- [19] C.J. Shih, *J. Eur. Ceram. Soc.* 19 (1999) 2773.
- [20] C.J. Shih, *Ceram. Int.* 26 (2000) 47.
- [21] L.P. Chen, K.L. Ying, K.C. Hsu, *J. Appl. Polym. Sci.* 92 (2004) 2232.
- [22] K.C. Hsu, K.L. Ying, L.P. Chen, W.C. Wei, *J. Am. Ceram. Soc.* 88 (2005) 524.