

Preparation of ZnO Thin Film by Electrophoretic Deposition(EPD)

Byungsei Jun[†]

Nano Materials Science and Engineering Department, Kyungnam University, Changwon 631-701, Korea

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ABSTRACT

The electrophoretic deposition(EPD) of ZnO nano-sized colloids is investigated by changing the colloid number concentration, applied force, and deposition time. The change of the colloid size in a suspension was examined by the different colloid number concentrations ($N = 3.98 \times 10^{13}$, $N = 3.98 \times 10^{14}$, and $N = 3.98 \times 10^{15}$) with an increase of the deposition time and applied forces. Deposition behavior was investigated by changing the applied fields (from DC 5 V to 50 V) and the deposition time (5 min to 25 min). The surface microstructures of the as-deposited films were investigated by SEM. The dried films were sintered from 850°C to 1,050°C for 2 h and then the microstructures were also explored by SEM. The agglomeration rate was enhanced by increasing the colloid number concentration of colloids. Colloid number concentration in a suspension must be rapidly decreased at higher values of the electric field. ZnO nano-sized colloids had the highest zeta potential value of over -28 mV in methanol. A homogeneous microstructure was obtained at colloid number concentration of $N = 3.98 \times 10^{13}$, applied DC field of 5 V/cm and 15 min of deposition time at an electrode distance of 1.5 cm. Under these conditions, the deposited films were sintered at 850°C and 1,050°C for 2 h. The results show a typical pore-free surface morphology of a uniform thickness of 400 nm under these experimental conditions.

Key words : ZnO, Nano, Colloids, Suspensions, Stability, EPD, Microstructure

1. Introduction

ZnO is a substance of extensive interest because of it is a low-voltage, piezoelectric and short wavelength optoelectronic material.¹⁾ The ZnO varistor is one important example that can be used to demonstrate a grain boundary segregation controlled electrical device. Sintered ZnO exhibits grain boundary solute segregation when doped with bismuth, which is associated with non-linear I-V characteristics.²⁻⁵⁾ And, more recently, thin films of piezoelectric materials such as zinc oxide have been extensively investigated and developed for use in micro-electromechanical system (MEMS) devices.⁶⁾

However much, ZnO is of interest for electronic devices, it is not easy to sinter this materials at low temperature. There are many problems to reach the theoretical density of ZnO at low sintering temperature because ZnO has high vapor pressure at elevated temperature. Many efforts to develop ceramic products for high technology systems have concentrated on obtaining green microstructures with uniformly packed, equiaxed, narrow size distribution powders and pores of interparticles. As with most suspension based processes, if a well dispersed suspension is used, EPD can result in a highly homogeneous cast with a high mechanical strength and a low surface roughness. Moreover, the EPD method is also well known due to the low equipment cost, high deposition rate, and easily controlled layer thickness, allowing for an even,

dense, and large deposition layer.⁷⁻¹⁰⁾ The EPD is a process whereby charged particles in a suspension are deposited onto an electrode of opposite charge under an applied electrical field. The process of EPD basically comprises two steps.¹¹⁾ The first step is the migration of charged particles in a liquid solvent by the action of an applied electric field. The second step is the coagulation of particles to form an adherent layer on the electrode. The migration velocity of nano-sized colloids in a suspension will be highly increased under an applied force. The chance of collision among colloids and volumetric occupation of colloids in a suspension should be enhanced as colloids are made finer. The volumetric occupation of particles increases in the same container when particles are ground. In this manner, the particle number concentration will also be increased. A high particle number concentration may give a non-uniform microstructure because of the irregular coagulation in a suspension. Until now, most the particle concentrations of solution for EPD have been based on weight. In this study, the number concentration concept for ZnO nano-sized colloids will be employed in order to explore how the green microstructure develops into a new regime during EPD. The agglomeration behavior and settling observation of the suspension under applied force will be examined to find the optimal EPD conditions, with a consideration of the colloid number concentration, the applied force and the deposition time in a suspension.

2. Experimental procedures

0.3 mol% Bi₂O₃-doped with ZnO colloids was prepared by use of the solution combustion method. The batch composition and the experimental procedure followed the spray combustion

[†]Corresponding author : Byungsei Jun
E-mail : bsjun@kyungnam.ac.kr
Tel : +82-55-249-2694 Fax : +82-55-248-5033

synthesis method.¹²⁾ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Aldrich Chemical Co. Inc., USA) and $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (98%, Junsei Chemical Co., Ltd) and $\text{CH}_6\text{N}_4\text{O}$ (98%, Aldrich Chemical Co. Inc., USA) were employed as the oxidizer and reducing agent, respectively, for this solution combustion synthesis. The solution mixture in a beaker was heated to 350°C and then, combustion was initiated at this temperature and the reaction finished in seconds. The products of 340 nm size was reduced to 100 nm by an attrition mill. Attrition milling was done under conditions of zirconia bead (0.3 mm), 800 rpm and milling time of 3 h. The lattice parameters of ZnO were identified as $a = b$ (3.25) and c (5.2050), and composition of ZnO of 98.299 wt% and Bi_2O_3 of 1.701 wt%. (0.3 mol% Bi_2O_3 -doped with ZnO). The electrodes consisted of a circular (1.27 cm diameter) Pt coated cathode disk (silicon wafer, N-100, LG siltron), which was held in a Teflon-coated holder placed parallel to a rectangular 2×3 -cm silicon wafer anode with an electrode spacing of 1.5 cm. A 250-ml beaker was used as the bath container. The suspensions were ultrasonically treated immediately before EPD. Deposit weights were obtained by weighing the Si wafer substrates before and after deposition experiments followed by drying at room temperature for 12 h. The change of the colloid size in suspension was examined by the different colloid number concentrations ($N = 3.98 \times 10^{15}$, $N = 3.98 \times 10^{14}$, and $N = 3.98 \times 10^{13}$) with a zeta potential analyzer (Zetasizer 3000HS, Malvern, U.K). The value of the colloid number concentration was calculated by use of the density, diameter and weight of ZnO colloids. Deposition behavior was investigated by changing the applied fields (DC 5 V to 50 V) and the deposition time (5 min to 25 min). Settling of suspension was also observed by changing the applied fields (from DC 5 V to 50 V) and the settling time (30 min). The surface microstructures of the as-deposited films were investigated by SEM. The dried films were sintered at temperatures from 850°C to $1,050^\circ\text{C}$ for 2 h; then, the microstructure was also explored by SEM.

3. Results and discussion

3.1. Suspension stability of ZnO nanoscale colloids

Giersig and Mulvany¹³⁾ reported that stable suspensions might give a dense homogeneous deposit on the substrate. This suspension stability can be the result of processes such as disorientation or ionization of surface groups on the particles, readsorption of potential determining ions, adsorption of ionized surfactants or isomorphic substitution.¹⁴⁾ Interactions that occur between charges fixed at the particle surface and those free in the solution are important to the stability of a colloidal system. With high potential, a thicker double layer is needed to avoid coagulation derived by the London van der Waals (LVDW) attractive forces that operate on close particle approach. Hamaker and Verwey¹⁵⁾ have observed this phenomenon in the strong adhering sediment in the suspension during EPD. They observed that deposited layers seem to be a viscous fluid. A suspension with low zeta potential forms a viscous deposit because of the unstable suspension. Koelemans and

Overbeek^{16,17)} proposed an electro-chemical mechanism of deposit formation based by DLVO theory. They found that an increase of electrolyte concentration can induce coagulation of the system. A dispersion is stabilized by an additive absorbed on the particles, which increases the repulsive forces due to electrical charging or the steric-hindering approach of particles. Colloids are agglomerated unless they are suitably deflocculated by mutually repelling charged double layers or unless the close approach of particles due to the steric-hindrance is physically prevented. The interaction of two particles with identical charged double layers has been examined by DLVO. Lyklema¹⁸⁾ reported that isomorphic substitution in non-aqueous solvent is restricted to clay because he considered the electrostatic stabilization during EPD. This provides information on the agglomeration of particles in the suspension since zeta potential is closely related to the particle's double layer thickness. In this study, a non-aqueous system was employed because ZnO has some solubility in water at room temperature. ZnO is hydrolyzed from $\text{Zn}(\text{OH})_2$ and H^+ ion in aqueous solution, which brings on dielectric loss. ZnO has to be dispersed in an organic solvent for this reason. Therefore, the suspension stability of ZnO was observed by use of methanol as an organic solvent. The repulsion energy of the suspension in this experiment was set to correspond to a zeta potential of about 25 mV, in order to minimize coagulation. The colloid size with an increase of the deposition time was measured by changing of different colloid number concentrations in the stabilized suspension in order to investigate the agglomeration behavior. Until now, most particle concentrations of solution for EPD have been based on weight. In this study, the particle number concentration was employed because the zeta potential value can change due to unexpected situations around nanoscale colloids. The short distance among colloids leads to thinner electric double layer thickness. The fact may be caused by the fact that the volumetric occupation of colloids is larger than that of micron size particles. This means that the mean free path of colloids in a suspension is shorter than that of micron size particles. With this condition, it is not easy to determine a precise zeta potential value, or to obtain a stable suspension. These difficulties were reasons why the number concentration concept had to be employed in this study. Agglomeration in a suspension may be randomly induced by Brownian motion and convection. The time for the half reduction of the colloid number was calculated by Smoluchowski's Equation (1). The equation is defined as the function of the half reduction time of particle number concentration ($t_{1/2}$):

$$t_{1/2} = \frac{3\eta}{4kT} \cdot \frac{1}{N} \quad (1)$$

where, η is the suspension viscosity, k is the Boltzmann constant, T is the temperature, and N is the particle number concentration. The half reduction time of the colloid number concentration is reduced as the colloid number concentration is increased. It is considered that the collision chance for colloids in suspensions is drastically increased. With consideration of the practical EPD deposition time in this study, the colloid number con-

centrations were prepared at $N = 3.98 \times 10^{15}$ (5 wt%), $N = 3.98 \times 10^{14}$ (0.5 wt%), and $N = 3.98 \times 10^{13}$ (0.05 wt%). The colloid number concentration was calculated through a consideration of the density, diameter and weight of the ZnO sample. Fig. 1 shows that the weight gain increased when the number concentration changed without any external force. The results show that agglomeration spontaneously formed in a suspension during EPD.

The average agglomeration rate was enhanced with the increase of the number concentration, as shown in Fig. 1. In the case of number concentrations of $N = 3.98 \times 10^{15}$, $N = 3.98 \times 10^{14}$ and $N = 3.98 \times 10^{13}$, the average agglomeration rate was calculated at 3.36 nm, 1.68 nm, and 0.08 nm per minute, respectively. It was considered that the chance of collision in the suspension was drastically enhanced as the concentration increased. Therefore, the $N = 3.98 \times 10^{13}$ colloid number concentration was chosen for this EPD process.

3.2. Influence of electric field strength on agglomeration of colloids

Thermal jostling due to numerous molecular impacts from the liquid moves the particles at random. This tends to break up weakly bonded flocs with no primary minimum or large barrier; however, thermal jostling can cause a weakly flocculated system to form strong flocs. When two large, opposed and parallel plates separated by some distance are immersed in a suspension and connected to a battery, the electrical field gradient draws particles with surface charge density toward the plate bearing an opposite electrical charge. The mean free path of the nanoscale colloids is much shorter than that of large colloids, which may enhance the collision frequency of the particles in such a suspension. Irregular agglomeration during the forming process can cause undesirable large pores during further drying and sintering stages. The strength of an electric field may affect the concentration of colloids in a suspension. Even in the absence of coulomb interaction, colloids can be agglomerated by an electric field.

In addition, the electric field induces an electric dipole moment in the particles. The resulting dipole-dipole interactions increase collision rates and produce different agglomerate structures. The agglomeration behavior of nano-colloids may

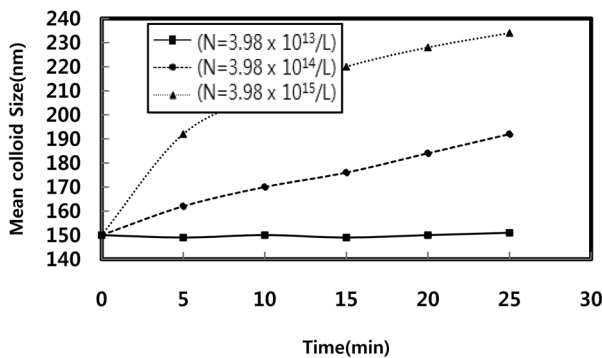


Fig. 1. Change of colloid size depends on the number concentration.

be strongly affected by these conditions, as shown in Fig. 2. Hirata,¹⁹⁾ and Zhang²⁰⁾ explained that weight gain was affected by the electrode area, particle mobility and particle concentration during the EPD process. The weight of the as-deposited films was increased with the increase of the applied electrical field. This can be explained by using Equation (2)

$$\frac{dw}{dt} = AuC \quad (2)$$

where w is the weight gain, A is a constant, u is the colloid migration velocity, and C is the colloid number concentration. It is well known that the particle mobility is directly enhanced by an increase of the applied field. Many pre-experiments have been conducted in this study to observe the optimum conditions for distance between anode and cathode. It is considered from the results of many experiments that the best condition for this system is 1.5 cm to form a uniform microstructure. The experiments were repeated with different applied electric field strengths. Fig. 3 shows the weight gain of particles on the substrate for the different electric field strength values.

The weight gain was gradually increased by the enhancing of the applied force from 5 V to 50 V, as shown in Fig. 3. The fact of this weight increase shows that the migration velocity of the colloid is faster as the applied force increases. The faster velocity may lead to irregular collisions among colloids in a suspension. With these conditions, a green state microstructure may have large size pores in the deposited film. There is no chance of obtaining a uniform sintered microstructure when a large pore is induced in a green deposit film.

3.3. Settling observation of suspension

Agglomerates may be naturally induced by collisions among colloids in a suspension when Brownian motion with convection exists. Colloids are agglomerated into clusters that themselves collide with other clusters and stick together. At the very beginning, the agglomerates are tiny and they move by diffusion.

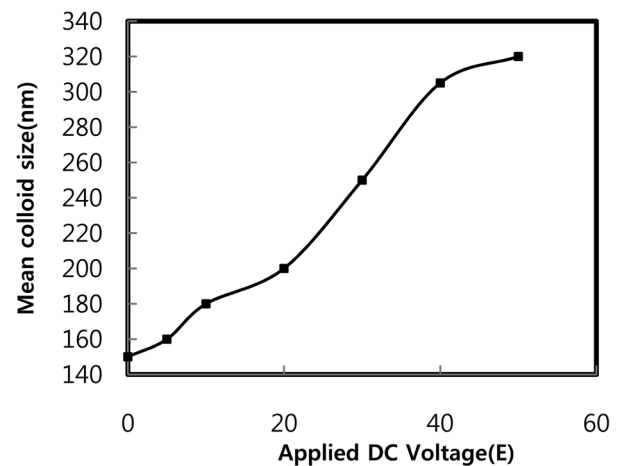


Fig. 2. Mean colloid size in suspension depending on applied forces.

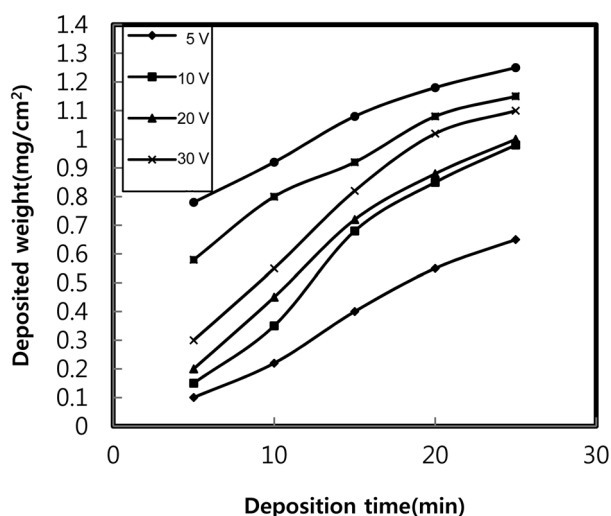


Fig. 3. Weight gain of deposited films depending on applied forces.

Later on, they grow to a large size and their settling velocity becomes significant. It is difficult to directly observe and quantify colloid-colloid interactions, so we usually determine the values for colloid parameters by measuring the motion of large particles when such large particles are exposed to an external force such as gravity or an electric field. In this study, the suspension was uniformly turbid when it was poured into the experimental cell. Nothing visible happened except that the turbidity increased significantly at the very beginning of the experiment, as shown in Fig. 4. The suspension appeared lumpy at 30 V and we were able to discern small aggregates of different sizes settling at different velocities. A large amount of agglomerate was observed and the top of the cell was starting to grow visible when the applied forces increased gradually from 5 V to 50 V, as shown in Fig. 4. With the 50 V condition, the turbidity of the suspension decreased and we were able to detect perfectly well-defined clusters settling separately in a clear fluid. The height of the sediment increased in the course of time and the top of the suspension progressively clarified.

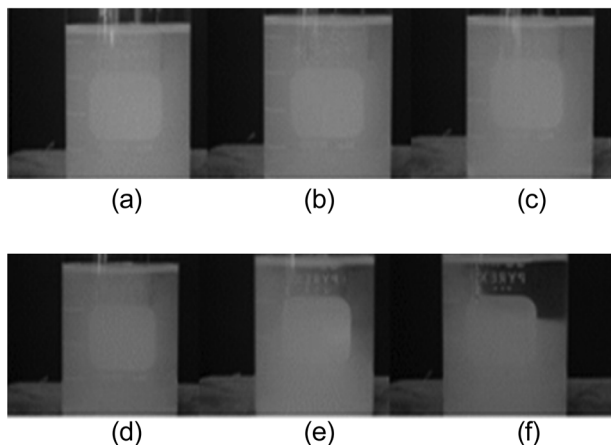


Fig. 4. Observation of settling in suspension (a) 5 V, (b) 10 V, (c) 20 V, (d) 30 V, (e) 40 V, and (f) 50 V.

The entire upper part of the suspension clarified at 50 V at the beginning of experiment, as shown in Fig. 4.

3.4. Applied force effects on green state microstructure of the film

After the electric field was turned off, film growth stopped as expected, but the film was able to maintain itself for a long time, even in the absence of an electric field. The mechanism of film growth on the substrate in suspension is not fully understood. It is necessary to account not only for the enhanced coagulation but also for the particle deposition on the electrodes. This may occur by Brownian diffusion and Coulomb attraction between charged particles and electrodes. The inevitable inhomogeneity of the electric field may also lead to a force that drives the particles toward the electrodes. For deposited colloids, a strong local electric field surrounding them may lead to an attractive force, which would cause further particle deposition. In this situation, colloids with charges moved fast toward the opposite electrode and collided with each other; they then agglomerated due to the applied forces. The microstructures changed to become porous with large pores due to the raising of the applied force, as shown in Fig. 5. This change to a state of large pores must be the result of the compaction of the large sized agglomerations. The side view of the film shows that the colloids were densely packed for a low applied force at 5 V in the suspension, as can be seen in Fig. 5.

From these results, the number of collisions among colloids in a suspension may be considered as lower at this low voltage. More time is needed to form a film at 5 V than at other voltages. The surface view of the film also shows an inhomogeneous microstructure at 50 V, as can be seen in Fig. 5. This is caused by the big agglomerates derived from the high electric field in the suspension.

This extends the mechanism proposed by Tai et al.,²¹⁾ who stressed the importance of particle growth due to enhanced coagulation. The observation of islands where particles grow on the electrodes supports the idea of a mechanism of enhanced deposition resulting from the inhomogeneous field surrounding the deposited particles.

3.5. Microstructure of sintered films

Fig. 6. shows the microstructure of the ZnO deposited films with conditions of $N = 3.98 \times 10^{13}$ concentration, applied force of 5 V, deposition time of 15 min, and distance of 1.5 cm, sintered at 850°C and 1,050°C for 2 h. Fig. 6(a) shows that the colloid coalescence and inter-colloidal neck formation is initiated at the intermediate stage of the liquid sintering. Fig. 6(b) shows that the grain boundary was composed, and then the pores disappeared at the final stage of the liquid phase sintering. At this temperature, eutectic liquid or Bi-rich liquid induced by Bi_2O_3 permits a fluidity, which leads to liquid sintering.

4. Conclusions

It is difficult to directly observe and quantify particle-particle interactions, so we usually determine the values for particle

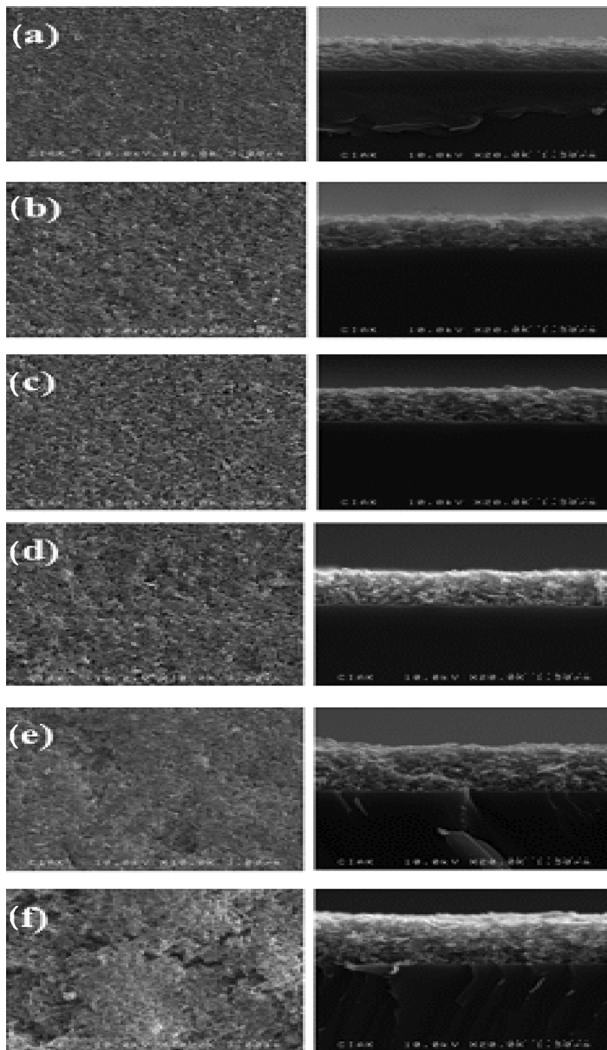


Fig. 5. Film in green state : left is top view, right is side view (a) 5 V, (b) 10 V, (c) 20 V, (d) 30 V, (e) 40 V, and (f) 50 V.

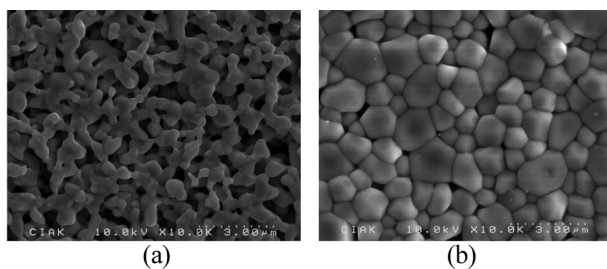


Fig. 6. Surface microstructure at different sintering temperatures (a) 850°C, (b) 1,050°C.

parameters by measuring the motion of large particles when those large particles are exposed to an external force such as gravity or an electric field. The weight gain of colloids with or without applied force was measured with an electrical balance. Colloid concentration in a suspension must rapidly decrease at higher values of electric field. A large amount of agglomerated

material was observed and the top of the cell started to become visible when the applied forces were increased gradually from 5 V to 50 V. The microstructures of the deposited films were starting to change into a porous state with large pores due to the increasing of the applied force. The side view of film shows that the colloids were densely packed for a low applied force at 5 V in suspension ($N = 3.98 \times 10^{13}$). The thickness of the film with good surface microstructure was 400 nm at 1,050°C for 2 h sintering condition.

Acknowledgments

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