

Pyrosol Generation of ZnO Nanoparticles and Structured Thin Films

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Abstract—Zinc oxide is a material of considerable research interest because of its properties eg photocatalysis, piezoelectricity. This paper describes the production of zinc oxide thin films, nanoparticles and combinations by the ultrasonic pyrosol process using a dual heater configuration.

Keywords; pyrosol; nanoparticle; zinc oxide; thin film.

I. INTRODUCTION

The characteristics of zinc oxide have lead to considerable research being undertaken into this material. Its piezoelectric, optoelectronic and photocatalytic properties mean that many researchers are actively investigating this material.

For the application of photocatalysis, a large active surface is required. Normal pyrolysis methods of dissociating precursors onto a hot substrate [1] can produce films with only a limited surface area. Deposition of nanoparticles from solution can increase the surface area. Production of nanoparticles however can also be made via the inexpensive ultrasonic spray pyrolysis (pyrosol) process when droplets pass through a heated zone before impinging on the substrate [2]. The size of the particle depends on the droplet size, concentration of precursor and temperatures used. In this paper, zinc oxide films of varying characteristics are produced by the pyrosol process with combinations of heat zone temperatures.

II. EXPERIMENTAL

Pyrosol deposition was performed using zinc acetate dihydrate (Merck) solution at concentrations below 0.1M in water. Substrates used were microscope slides ultrasonically cleaned in detergent solution and/or cleaned with an abrasive plastic pad before rinsing in water, DI water and air-blast dried.

The ultrasonic pyrosol system consisted of a ~1MHz generator (TISTR) coupled through a stabilizing water jacket to a plastic container holding the sample liquid as illustrated in Figure 1. Approximately 30ml of solution was placed in the container and the ultrasonically generated aerosol was transferred through a ~25mm diameter stainless steel tube by means of very low pressure compressed air at a flow rate of less than 1L/min. The emerging vapour was directed either

toward a heated glass substrate placed on a hotplate or to a 100ml beaker filled with deionised water. A second hotplate was placed below and coupled to the stainless steel tube near the sample substrate and was able to be heated to ~400°C to either preheat the emerging droplets or to evaporate the water solvent so that hot solid particles emerged from the tube. Temperatures were measured by K-type thermocouples. SEM images were obtained on either a JEOL FESEM JSM6340F (TISTR) or JEOL JSM6301F (MTEC).

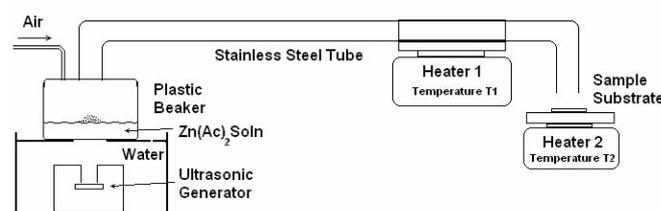


Figure 1. Pyrosol deposition system using two heaters.

III. RESULTS AND DISCUSSION

When the temperature of the tube heater (1) was at room temperature with substrate heater (2) hot (~400°C), decomposition occurred on the substrate and Figure 2 shows the SEM image of the film formed for T2 = 400±20°C.

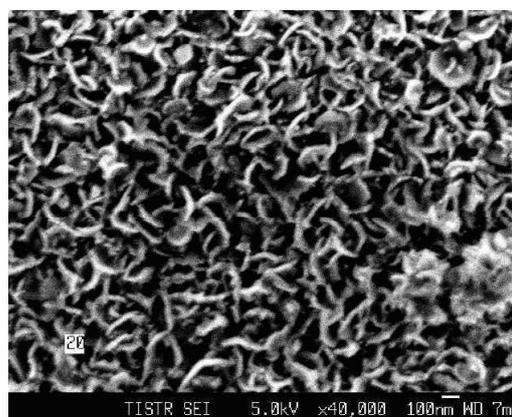


Figure 2. SEM image of T1 low, T2 high film

In 30 minutes of deposition a film of ~750nm, as measured by a Dektak profilometer, was formed from a starting solution of 0.1M Zn(Ac)₂. The perpendicular to substrate growth of “cauliflower” like structures [3] shows the growth characteristics of ZnO which is known to have many orientations [4] especially when deposited from an aqueous environment.

For tube heater (1) at ~400°C, the zinc acetate solution was decomposed and solvent vapourised during transit through the tube emerging as a solid particle of ZnO. A beaker of water was used to capture the particles.

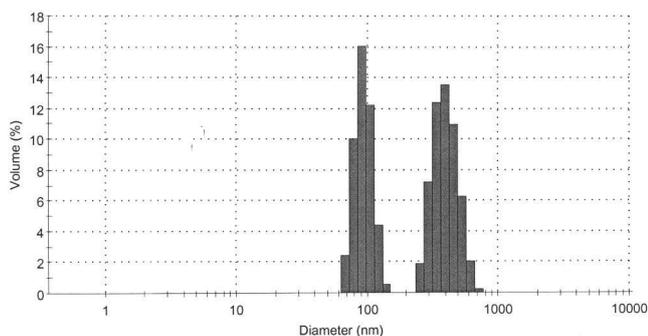


Figure 3. Particle sizing for 0.1M Zn(Ac)₂ sample

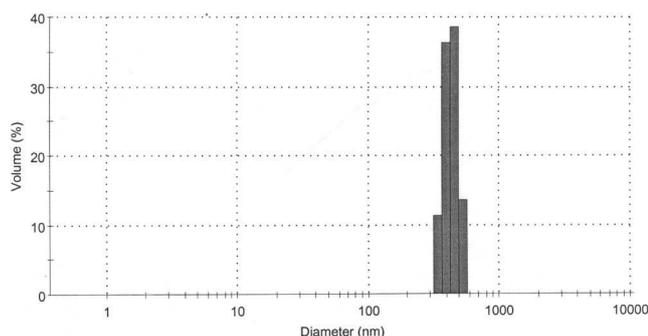


Figure 4. Particle sizing for 0.03M Zn(Ac)₂ sample

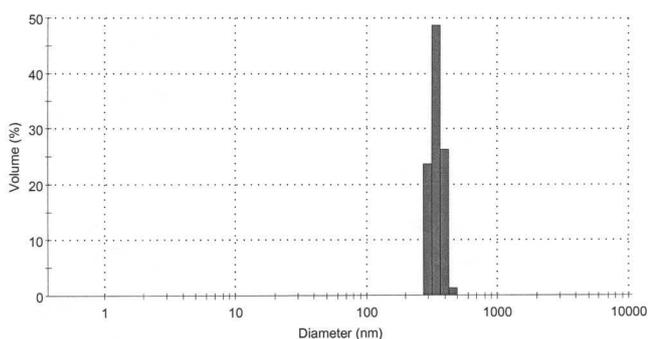


Figure 5. Particle sizing for 0.008M Zn(Ac)₂ sample

After filtering with filter paper (Whatman No.1 11micron) particle sizing by volume, using a Malvern Zetasizer NanoZS, measured particles of 80-120nm and 300-600nm for 0.1M, 200-500nm for 0.03M and 150-300nm for 0.008M zinc acetate

solutions. These values agree with calculations for an aerosol particle size of near 5 microns.

The temperature T1 for the 0.1M Zn(Ac)₂ sample shown in Figure 3 was noted to be below 350°C for a significant fraction of the collection time. This may explain the two particle distribution in Figure 3.

Figure 6 displays the SEM image of particles produced from a similar process with 0.1M Zn(Ac)₂ starting solution and tube heater (1) at ~390°C while substrate heater (2) was at 140°C. This image displays a range of particle sizes from 0.5µm to 1.5µm diameter which may result again from slight variations in T1. Also apparent and shown more clearly in Figure 7 are the smaller subparticles of ~30nm diameter which agglomerate on the evaporation of the water to make the larger particle and the hollow nature of some particles leading to large surface area and porosity.

These subparticles appear to arise from the hydrolysis of the zinc acetate solution which is heated as it passes through the stainless steel tube. Control of the particle characteristics could be achieved by adjusting solution concentration, ultrasonic droplet size, tube temperature and residence time.

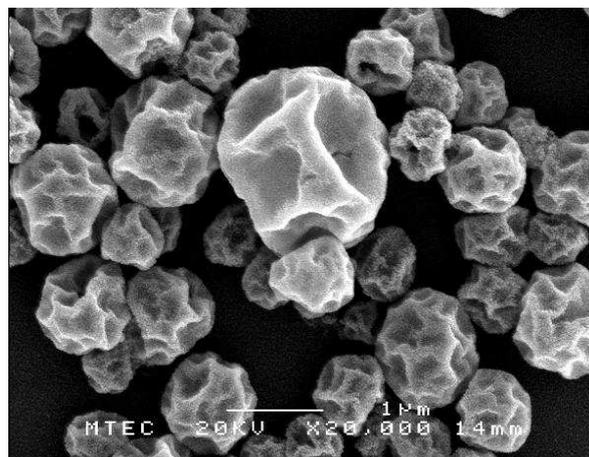


Figure 6. SEM image of T1 high, T2 low deposit

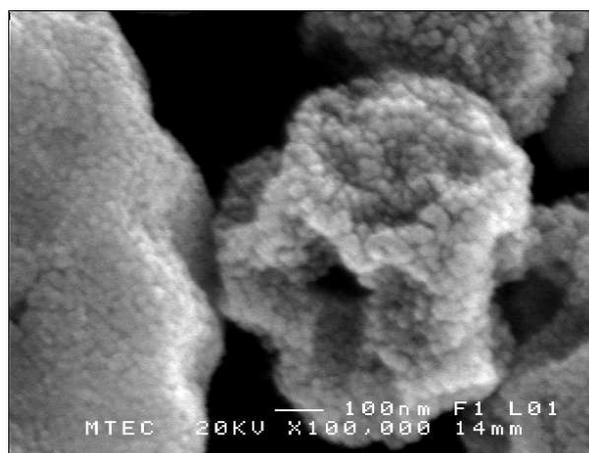


Figure 7. SEM showing agglomerated particles.

Zinc Oxide nanorods can be formed when T1 is at an intermediate temperature ie. less than 300°C and T2 is high ie. above 320°C as shown in Figure 8. Here the SEM image displays nanorods again formed from an approximately 30nm subparticle with ~5 particles per nanorod. These may result from the deposition of droplets containing small particles formed by hydrolysis during transit through the heater 1 region. Final evaporation of the water droplet on the substrate results in agglomeration of only a few subparticles into nanorods of ~5 particles.

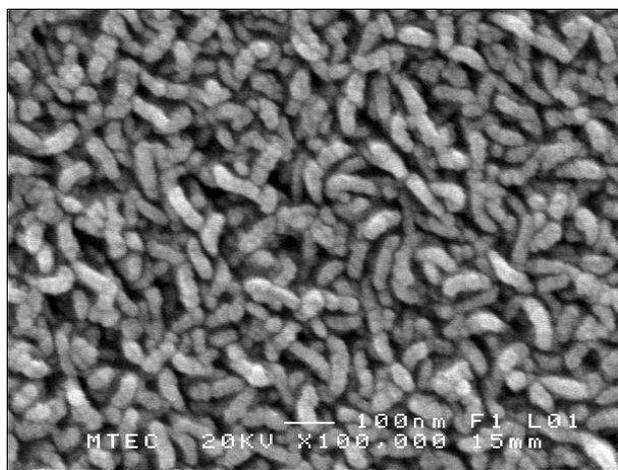


Figure 8. SEM image of T1 med, T2 high film.

Figure 9 shows the result of a multiple temperature regime where both T1 and T2 were adjusted to create particles (T1 high, T2 low) and nanorods (T1 intermediate, T2 high) on the same substrate.

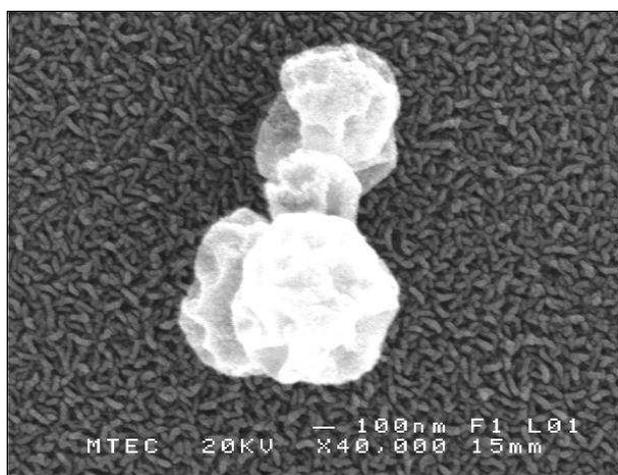


Figure 9. SEM image of T1,T2 sequenced deposit

XRD spectra (JEOL JDX-3530) of the crystal structure of the films restricted to the (002) ($2\theta=34.4^\circ$) and (101) ($2\theta=36.2^\circ$) regions are displayed in Figures 10 and 11. The

peak positions correspond well to those expected for Zincite (ZnO mineral from ICDD database) with variation observed in the ratio of the peak heights for T1 low, T2 high (cauliflower) and T1 med, T2 high (nanorod). This variation can result from orientation or dopant effects[5].

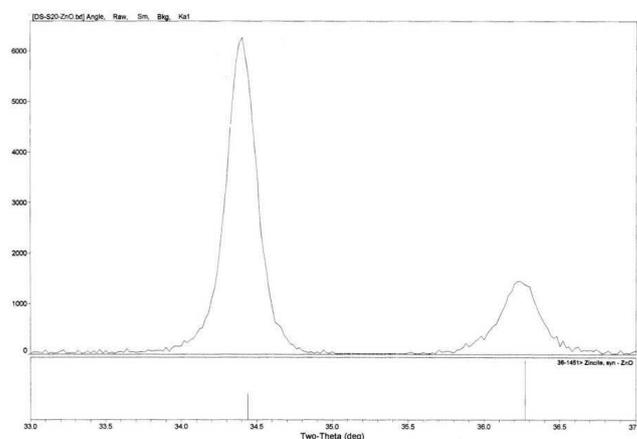


Figure 10. XRD spectra for T1 low, T2 high film

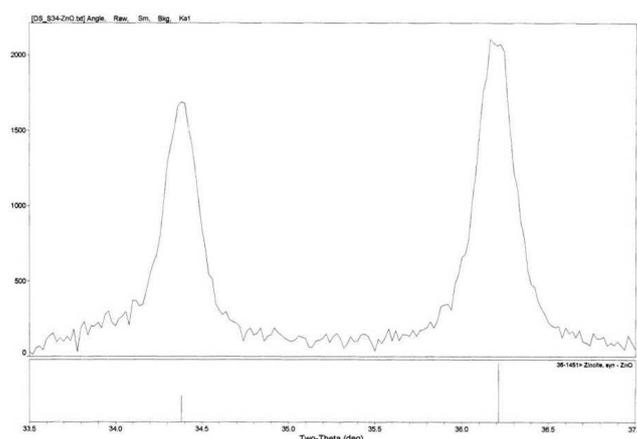


Figure 11. XRD spectra for T1 med, T2 high film

The width of the XRD peaks is an indicator of crystallite size or lattice strain and from the data, sizes of 33-43nm for sample T1 low, T2 high and 35-45nm for sample T1 med, T2 high were determined. These correspond well to the size of features and subparticles observed in Figures 2 and 8.

IV. CONCLUSION

The combination of two process temperatures enables films with differing properties to be deposited. By adjusting the time duration it should be possible to create a larger number of large particles (~1 μ m) and subsequently deposit nanorods to coat these for enhanced surface area. This may also provide improved particle adhesion to the substrate. Provided the surfaces are active[4], which may be modified by using different solvents and carrier gases[5], the enhanced surface area from this process could increase photocatalytic activity.

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