Gas-Phase Nanoparticle Dynamics during Laser/Aerosol Synthesis of Zinc Oxide Nanocrystals

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Abstract: Aerosol processes provide a flexible platform for controlled generation and deposition of gas-borne ZnO nanocrystals and their integration into nanoparticle-based systems with complex architecture. In this work we have combined laser synthesis and on-line aerosol processing to improve control over the synthesis of ZnO nanostructures. We have used the aerosol technique known as differential mobility analysis to perform high-resolution particle spectrometry in the 1-60 nm size range and study the gas-phase dynamics of nanoparticles formed during KrF pulse laser vaporization of ZnO targets. These targets are vaporized in inert gas atmosphere with background pressures in the 70-760 Torr range and laser fluences of 1-6.25 J/cm2. Measurements reveal that during ZnO vaporization at relatively low laser fluences (<1 J/cm2) the gas-suspended nanoparticle population that ensues exhibits lognormal size distributions with a concentration peak in the 5-10 nm size range. As the laser fluence increases above 2 J/cm2 the peak of the distribution shifts to diameters well above 20 nm. By adjusting the inert background pressure, the laser energy density, and the aerosol dilution rate, we have been able to monitor and control the aggregation process of these gas-suspended ZnO nanoparticles for delivery to selected locations on a substrate and potential integration into functional systems. We acknowledge support from the National Science Foundation (NSF)-Research Experiences for Undergraduates (REU)-site award to the University of Alabama at Birmingham (UAB) under Grant No. DMR-0243640, and Major Research Instrumentation Grant, No. DMR-0116098.

Introduction

Zinc Oxide (ZnO) is a promising wide bandgap semiconductor for applications in UV light emitting devices and sensors. For several years ZnO research has focused intensely on optimization of bulk and epitaxial growth, p-type doping, and production of high quality metal contacts. [8] More recently these efforts have expanded to include synthesis, properties, and device integration of ZnO nanostructures. A variety of such low-dimensional structures (e.g., nanocrystals, nanowires, nanohelixes, nanotubes) have been demonstrated exhibiting greater purity and better crystal quality than bulk crystals and epilayers, as low defect concentrations are statistically favored in these nanoscale systems. [8] These nanostructures present potential for important applications particularly in biosensing devices and other nanoscale transducers. A challenging problem facing this area however involves the controlled assembly and integration of these nanoscale objects into anisotropic and highly functional systems of complex architecture.

Zinc Oxide (ZnO) has caused a great deal of interest in finding the capabilities this material have. ZnO is a unique material that demonstrates semiconducting, piezoelectric, and pyroelectric material. [8] This material can be found in aerosols. Aerosols are a particle suspended to a gas. Aerosols can be harmful and helpful to the human body, depending on the size of the particle and the material that has been suspended into a gas.

ZnO has a mass density of 5.6 grams/cm^3 and an atomic density of 8.87 $\times 10^{22}$ atoms/cm^3. Zinc oxide has a nano crystal structure that has a repeated pattern between the Zinc and the Oxygen molecules. This nanocrystal structure is most likely the richest family of nanostructures among all one-dimensional nanostructures.

The mixture of ZnO materials with KrF pulsed lasers, have become a widely observed phenomenon. There have been numerous times that laser ablation are treated as an undesired feature to be minimized or, if possible eliminated. However in aerosol science, laser ablation in ambient gases provides an efficient way of producing aerosols with a broad range of properties. There have not been many studies to date that have focused on the use of this technique as a source to intentionally generate a stable, controlled, and well characterized aerosol of fine and ultra fine particles for nanostructure and particulate engineering applications.

There are characteristic such as experimental simplicity, materials versatility, and reproducibility of complex target stoichiometry, afford interesting prospects for the use of laser ablation aerosols in engineering systems. However there are many details that are involved in the behavior of aerosols that are not yet understood. For example, multiple excitation pathways resulting from the laser-target interaction lead to the generation of a complex initial state comprising ions, cluster, particles, and droplets. [1] Understanding the fundamentals of the aerosol process that takes place during the formation and evolution of this material is necessary if laser ablation is to be optimized and tailored to the synthesis of nanostructures materials via aerosol routes.

The Zinc Oxide aerosol particles were obtained by the ablation of a solid ZnO target. The high pressure DMA was used to measure the aerosol size distribution into eh 1-60 nm range while the Aerosol Electrometer collected the particles and provided information on the particles size.

There is a strong possibility that ZnO could be applied to optoelectronics, sensors, transducers, and biomedical science. Proving this will be very beneficial because it is bio-safe, biocompatible, and can be grown on cheap substrates such as glass. Also understanding the behavior of ZnO materials is important for the fight against skin cancer from the ultraviolet rays.

Experiment

A schematic of the experimental apparatus utilized in this study is depicted in Fig 1. Nitrogen and argon gas were pumped through mass controller flows at set values. Inside the cylindrical device the ZnO pressed powdered target was vaporized in inert gas by KrF excimer laser at atmospheric pressure. Laser fluences of 1-6.25 J/cm2 were used. The experimental parameters were used was to adjust the inert background pressure, laser energy density, and the aerosol dilution rate. The system allows a vertical displacement of the target to ensure long-term stability of the aerosol population. The aerosol is generated by the ablation of the ZnO target using the focused beam of a pulsed laser:

KrF (248 nm emission wavelength, 5 Hz repetition rate).

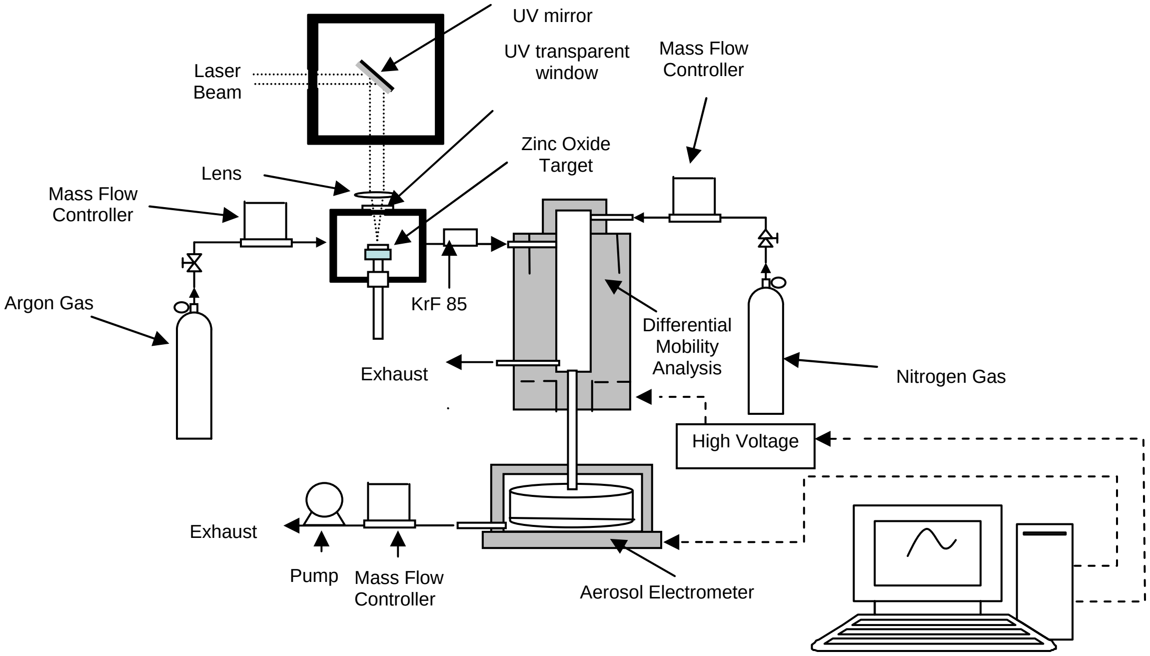

Fig.1. Schematic of the experimental apparatus used for the synthesis and characterization of laser ablation aerosols. There was a laser wavelength of 248 nm and a laser fluence of 1- 6.25J $cm^{-2.}$

The aerosol particles formed where then ran through an ^{85}KrF neutralizer and enter into a Differential Mobility Analyzer (DMA) for mobility measurements. After passing through the DMA the passing particles are introduced to the Aerosol Electrometer where data on the particle size is provided. The provided data is displayed on the computer.

The DMA used in this experiments is a cylindrical instrument made after the Vienna DMA. [1] Its geometrical parameters are R_1 = 25 mm, R_2 = 32 mm and L = 188 mm, where R_1 and R_2 are the diameters of the inner and outer electrodes, and L is the length of the classified region.

The DMA was operated with aerosol mass flow rates of 1 SLM (standard liter per minute) of argon and 5 SLM of Nitrogen allowing measurements of the aerosol size distribution in the 1-60 nm range at 70-760 Torr. These flow rates remained constant during measurements by the mass flow controllers and the system pressure were adjusted through manual valves. Inversion of the mobility data was placed onto a equilibrium charge distributions calculated according to Fuchs theory with the pressure dependence of the ion properties taken into account as suggested by Seto. [1] Size distributions have also been corrected based on independent measurements of particle transmission as a function of size and pressure.

Measurements were performed for laser fluences of the target surface between 1and 6.25J cm^{-2}. The laser beam was focused to a spherical spot of the ZnO, with a diameter of .02 cm^2. The ambient pressure varied in the range 75-760 Torr.

Results and Discussion

Normal characteristics of the aerosol

Within the range of experimental conditions tested, mobility measurements on the aerosol generated during ablation of ZnO revealed consistent size distributions. An example can be seen in Fig 2 for laser fluence 1- 6.25 J cm^{-2} and a pressure of 75-760 Torr. For these conditions, it was found that the measured size distributions reproduced a log-normal distribution, which were consistent with the DMA transfer functions. A best fit was obtained when the log-normal function had a geometric mean diameter of 26 nm (Dpg), with a geometric standard deviation $\sigma_g \approx 1.7$

Fig.3. Illustrates reproducibility of the size distributions under the same conditions (6.15 J cm^{-2} and a pressure of 75-760 Torr). The size distribution increases slightly as the diameter of the particle are raised (D_p). The peak on each measurement is all closely consistent.

Fig.4. Shows the size particle distribution tested under different laser energy conditions but the pressure remained constant (1- 6.25 J cm^{-2} and a pressure of 75-760 Torr). It illustrates the decreasing of the size of particles after 6.15 J cm^{-2}. However little significance can be attributed to the data after the 6.15 J cm^{-2}.

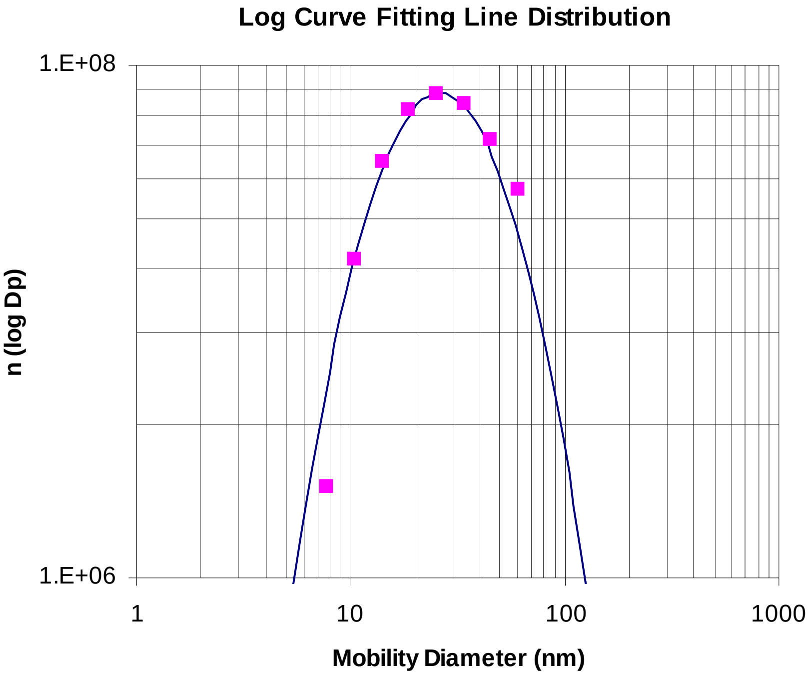

Fig. 2 this is a typical aerosol size distribution measured by a differential mobility analyzer. The solid line fitted to the data points represents log-normal distributions. The Log-normal function had a geometric mean diameter of 26 nm with a geometric standard deviation σ_g=1.7

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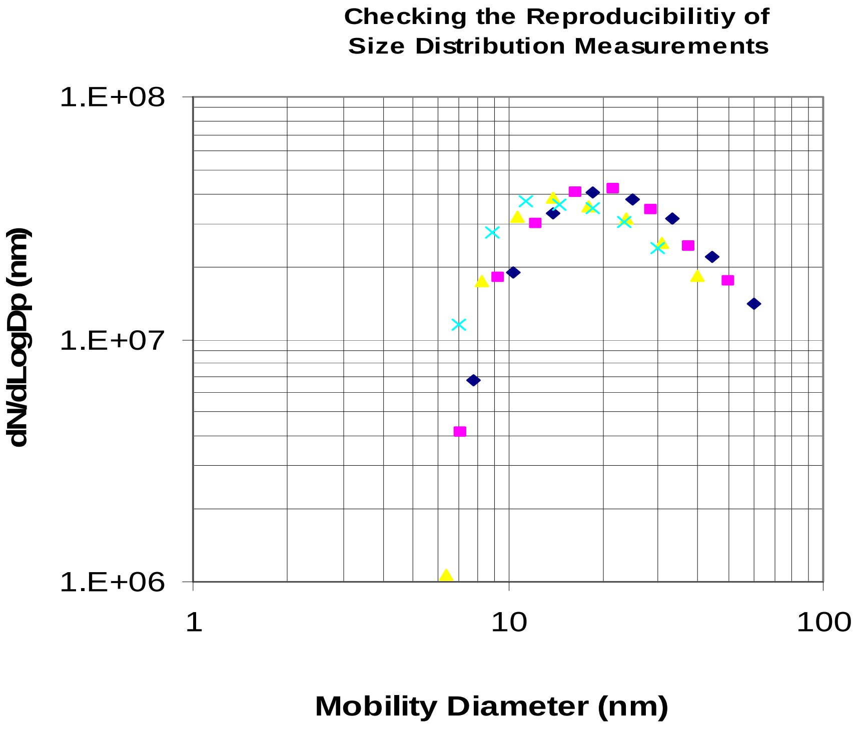

Fig. 3. This is a reproducibility graph, illustrating aerosol size distribution measured by a differential mobility analyzer while under the same conditions. 6.15 J cm^{-2} and a pressure of 75-760 Torr. The diameter of the particle changes but each distribution peaks around 20-25 nm.

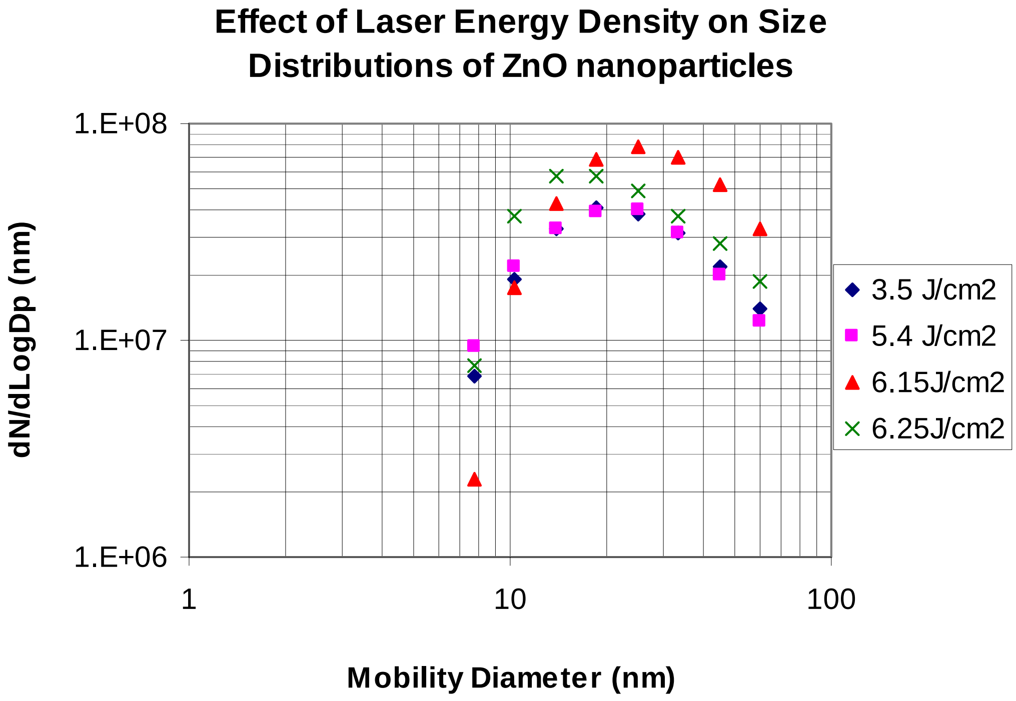

Fig.4. Displays data aerosol size distribution under different laser energy density, however the pressure, which was 75-760 Torr, remained the same.

As the ambient pressure varied, the concentrations of the aerosol size distribution particle change as noted in figure 4. The number of particles seemed to increase with pressure. Since the most important parameters are fixed, namely the laser wavelength and the laser fluence, this observation suggests that a mechanism involving the ambient gas is responsible for the particle formation. If this argument proves to be correct ambient gas with online laser ablation may be use to control the size distribution of ZnO nanoparticles.

Besides the laser wavelength, laser fluence is usually regarded as the most important parameter in the formation of particulate material during laser ablation. Understanding the importance in the particle generation, we measured the effect of laser fluence on the aerosol size distribution. Figure 4 displayed how the size distribution changes as a function of the laser fluence for the ambient pressure.

For the particles, the average particle size seems to be independent of laser fleunce in the range measured.

ZnO Aerosol Formation and Evolution

The modal size distributions often arise due to the operation of distinct mechanisms of particle formation.

The initial principal that governs aerosols formation is the generation of supersaturated vapor of the ZnO material. At high supersaturation, the vapor will nucleate into a large number of small particles. [9] These nuclei act as seeds for particle growth by condensation or other vapor deposition process as they simultaneously undergo rapid coagulation. In the beginning when the particles are still quite small, coagulation is followed by rapid coalescence. After undergoing this process, dense particles begin to be formed. This processes of nanoparticle growth is displayed in figure 5.

As the aerosol cools, the particles begin to grow large enough that they can no longer coalesce completely between coagulation events. If this happens, the aerosol will evolve into a population of aggregates with a complex fractal-like structure. [8] Precise control of the ZnO crystallite size is possible only in the early stage of dense particle growth.

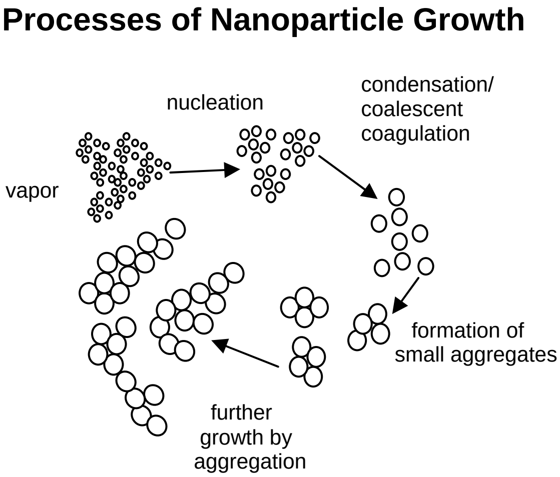

Fig. 5. Illustrates the nanoparticle growth. As the nanoparticles reproduce into large amounts they began to get bigger by nucleation, coagulation, and aggregation.

ZnO nanostructures by laser ablation

During the laser ablation process the energy source is located outside the vaporization chamber, it is decoupled from the gas flow. The amount of vaporized material is less dependent on target erosion and flow variations, which makes laser ablation a more reproducible means for the synthesis of ZnO nanocrystals.

Also during laser ablation the area from which the ZnO material is evaporating can be precisely controlled, decreasing the risk of contamination. This is very important because during spark ablation, sparks may occasionally hit metal parts, causing undesired vaporization of other species. [8]

Log-Normal Size Distribution Function

The Log-Normal function is commonly used to characterize the size distribution of atmospheric particles and emissions. The log-normal distribution is a continuous random variable resulting from transforming the normal distribution with the exponential function Using the log normal function makes it an advantage to find a curve fitting line because there are only two parameters, the median diameter and the geometric standard deviation, that are required to define it. Also the cumulative distribution plots as a straight line on logarithmic excel program. In addition, if the distribution by mass is a log normal function, the surface area distribution and the number distribution are also normal with the same geometric standard deviation as displayed in figure 6.

The log-normal function that was used on figure 2 can be seen in figure 6b.

Unlike Guassian function, the log-normal function is asymmetric. The two function look similar. However the log-normal function has the ability to display a sudden drop or a slowly decreasing drop on a logarithmic scale, which is illustrated in figure 7. Whereas the Guassian function drop is very narrow and sudden.

The log-normal size distribution function in figure 6. shows the relation of its function related to the online laser ablation data in figure 2. As the laser ablation increase, the size and number of particles increase. As illustrated in figure 6. The width of each curve remains equal despite the increasing of ZnO nanoparticles.

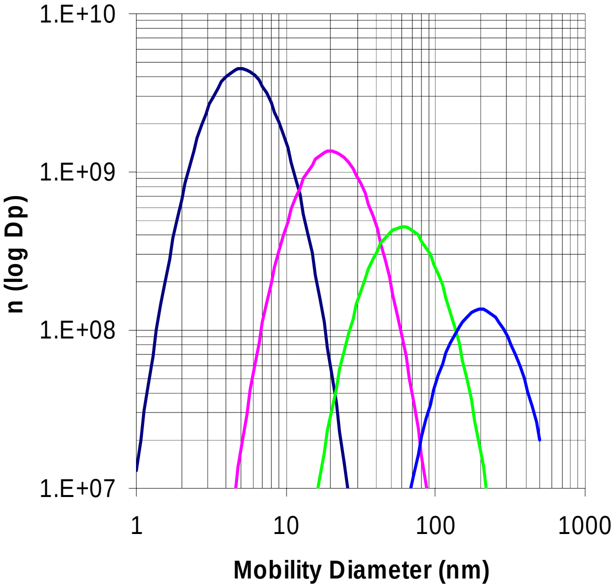

Figure 6. Demonstrates the lognormal functions and the pattern that it undergoes with the ZnO material. As the laser energy density increases, the number of particles increases also.

$$n\left(\ln D_p\right) = \frac{N}{(2\pi)^{1/2} D_p \ln\sigma_g} \exp\left[\frac{(\ln D_p - \ln \bar{D}_{pg})^2}{2\ln^2\sigma_g}\right]$$

Figure 6b displays the log-normal function that was used to fit the ZnO size distribution data show the reproducibility graph.

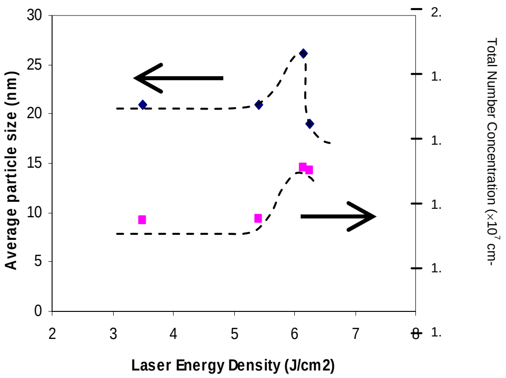

Figure 7. Illustrates the experimental trend of the schematic. Arrow 1 pointing to the right it showing the average size of the particle (nm) as the laser energy density increases (J/cm2). While arrow 2 is displaying the total number of concentration particles ($\times 10^7 cm^{-3}$) with respect to the laser energy density (J/cm2).

Summary

We have explored the use of a high differential mobility analyzer to study aerosol formation during laser ablation. This study has shown that the differential mobility analysis may be used successfully in combination with laser ablation to monitor the formation and evolution of Zinc Oxide material during in the gas phase.

Our model aerosol was generated by 248-nm pulsed KrF.: YAG laser ablation of solid zinc oxide. The results of mobility measurements show that the aerosol peak ranges from 20-26 nm.

There is a strong possibility that this may allow better control of laser synthesized ZnO nanostructured films for potential integration into functional system

Future Work

With Zinc Oxide growing rapid interest we will conduct future work to gain further knowledge on this material. Future experiments consist of testing the Zinc Oxide with online-laser ablation at higher pressure and laser fluences.

There is a possibility that after 6.25 $J/cm^{-2,}$ instead of the size distributions continuing to grow they began to decrease. We do not know for sure whether the nanoparticles size distributions decrease or increase.

Another possibility is the increasing and decreasing of ambient pressure. It is a fact that the ambient pressure has an affect on the size distribution of particles. However we do not know how much affect it will have if we increase or decrease the pressure, while keeping all the other parameters the same.

ZnO Future

With Zinc Oxide becoming a favorable semiconductor with its wide direct bandgap of 3.3ev there has been much interest in optoelectronics applications to use this material as a UV laser. [2,4] Zinc Oxide is a strong candidate for short-wavelength optical devices such as laser emitting diodes or laser diodes.

Zinc Oxide in the usage of thin films has shown very strong spontaneous and stimulating emissions by excitons at room temperature. [3,6] This versatile material is also being used or considered for antireflections coatings, transparent electrodes in the solar cells, gas sensors, varistors, surface acoustic wave devices, electro and photoluminescent devices, and is considering promising for phosphor for low-voltage luminescence in flat panel displays. [4,7]. However there is no clear understanding of defect-related luminescence phenomena in ZnO. [5]

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References:

[1] Camata P. Renato, Hirasawa Makoto, Okuyama Kikuo, and Takeuchi Kazuo (1999) Observation of Aerosol Formation During Laser Ablation Using A Low-Pressure Differential Mobility Analyzer, J. Aerosol Science Volume 31, No. 4, pp.391-401, 2000

[2] Jin J.B., Woo, S.H, S. Im, Bae H.S., Lee Y.S., (1999) Relationship between Photoluminescence and Electrical Properties of ZnO Thin Films grown by Pulsed Laser Deposition, Applied Surface Science 169-10 (2001) 521-524

[3] Ryu R.Y., Zhu S., Look C.D., Wrobel M.J., Jeong M.H., Whie W.H. (2000) Synthesis of p-type ZnO films, Journal of Crystal Growth 216 (2000) 330-334

[4] Jin .J.B., Im S., Lee S.Y., Violet and UV luminescence emitted from ZnO thin films grown on sapphire by pulsed laser deposition, Thin Solid Films 336 (222) 107-110

[5] Hur Bong-Tae, Jeen Soo Gwang, Hwang Hwae-Yoon, and Kim-Kook Hyung (2002) Photoluminescence of polycrystalline ZnO under different annealing conditions, Journal of Applied Physics Volume 94, Number 9

[6] Makino T., Chia .H.C, Segawa Y., Kawasaki M., Ohtomo A., Tamura K., Matsumoto Y., Koinuma H., (2002) High-throughput optical characterization for the development of a ZnO-based ultraviolet semiconductor-laser, Applied Surface Science 189 (2002) 277-283

[7] Studenikin A. S., golego Nickolay, and Cocivera Michael, (1998) Fabrication of green and orange photoluminscent, undoped ZnO films using spray pyrolysis, Journal of Applied Physics Volume 84, Number 4

[8] Wang Lin Zhong, (2004) Nanostructures of Zinc Oxide, Materials Today

[9] Camata P. Renato, PhD thesis California Institute Technology (1998) Aerosol synthesis and manipulation of semiconductor material.