**Excimer laser accelerated hydrothermal synthesis of ZnO nanocrystals
& their electrical properties**

**K. D. G. I. Jayawardena*, Charles Opoku, James Fryar, S. Ravi P. Silva
and Simon J. Henley**

Advanced Technology Institute, University of Surrey, Guildford, GU2 7XH, UK

*Corresponding author : k.jayawardena@surrey.ac.uk

The synthesis of ZnO nanocrystals is reported using a hydrothermal chemical growth technique combined with 248 nm nanosecond excimer laser heating at fluences in the range 0 – 390mJ cm⁻². The effect of laser heating in controlling the morphology of the nanocrystals is investigated using optical spectroscopy and electron microscopy characterization. Laser heating is shown to allow control of the crystal morphology from nanoparticles to nanorods as well as to modify the size distributions. The results indicate that not only does the laser accelerate the growth of nanocrystals, but can also produce crystals with a narrow size distribution possibly via photothermal size selection. An initial study of electrical conduction properties of ZnO nanocrystal thin films is also discussed.

1. Introduction

Among the semiconductor nanomaterials that are currently actively investigated, ZnO has attracted considerable interest among the research community. The wideband gap (3.3eV) as well as the high exciton binding energy (60meV) of bulk ZnO makes this a material with potential application for electronics as well as optoelectronic device physics.[1]

Traditionally, the growth of ZnO nanocrystals involves the use of high temperature synthesis techniques. However, hydrothermal synthesis which allows preparation of nanostructures at a lower temperature has begun to attract the attention of the research community due to its possible incorporation into device fabrication. [1],[2] Although temperature remains an advantage in this process, the longer growth time required combined with the difficulty in achieving morphology control prevents this technique from industrial implementation. This has resulted in new techniques such as microwave assisted hydrothermal growth.[3] In the work reported here, we describe how a 248 nm UV laser can be used to both control the morphology and accelerate the growth.

2. Experimental technique

Preparation of ZnO nanocrystals was based on the mixing of 2 ml of 25mM $\text{Zn}(\text{NO}_3)_2$ into a beaker containing 2ml of 25mM hexamethylenetetramine (HMTA) in D.I. water. Prior to mixing, both of the above precursors were heated upto 90°C in a water bath. Several solutions prepared in this manner and maintained at 90°C were irradiated with a 248nm KrF excimer laser using a repetition rate of 40Hz with fluence in the range of 0 – 390mJ cm⁻². Individual solutions were irradiated at each fluence for 5, 7.5, 10, 12.5 and 15 min. Completion of the irradiation process was followed by quenching of the

products to room temperature and centrifugation and redispersed in water to prevent aging. Characterization of the nanostructures formed was carried out using Philips XL30 SEM and Philips CM200 TEM. Optical absorption spectroscopy of ZnO nanocrystals in D.I. water was carried out using a Varian Cary 5000 UV-Vis spectrometer with the aid of a quartz cuvette with a 1cm beam path.

Subsequent to the characterization of the optical properties and the morphology of the synthesized crystals, I-V characteristics of thin films of ZnO nanoparticles prepared at 330 mJ cm^{-2} for 10min were studied using an interdigitated electrode (IDE) structure with a finger spacing of $2.5 \text{ }\mu\text{m}$ and Au electrodes. An Agilent 4142B was used for the electrical characterization. The thin film was obtained by a drop casting process followed by annealing at 443 K.

3. Results and discussion

SEM images of the samples prepared without laser irradiation (figure. 1) reveal that over a period of 5 – 15 min, the hydrothermally grown mixtures produce large microcrystals which change their morphology from a “diamond shape” to a more uniform cross sectional one with little change in the length. On the other hand, observation of the TEM images of the solutions grown with the assistance of the excimer laser reveal a distinct difference in morphology at fluences of 170, 330 and 390 mJcm^{-2} . At the lowest fluence of 170 mJcm^{-2} [figure. 2 a) & b)], the morphology of the samples are seen to change from more particle shaped at 5 min to a mixture of rods and particles at 15 min with a broad size distribution apparent in each case. On the other hand, when the fluence is increased upto 330 mJcm^{-2} , the morphology has remained particle like irrespective of the growth time [figure. 2 c) & d)]. When the fluence has

been further increased upto 390 mJcm^{-2} , the product is seen to consist of a variety of nanostructures ranging from particles to bi/tri/tetra-pods [figure. 2 e)].

The optical absorption spectra (figure 3) of ZnO nanocrystals prepared using 170 mJ cm^{-2} (5 and 15 min), 330 mJ cm^{-2} (5 and 15 min) and 390 mJ cm^{-2} (5 and 15min) reveals evidence in support of the features observed from the electron micrographs as well as an insight into the growth mechanism. At 5min for the lowest fluence of 170 mJcm^{-2} , the spectra display the presence of the ZnO band edge absorption closer 380 nm as well as an additional peak at $\sim 300 \text{ nm}$ which is due to unreacted $\text{Zn}(\text{NO}_3)_2$. Increasing the time upto 15min has led to the disappearance of the latter peak. However, an additional broad peak has appeared at $\sim 400 \text{ nm}$ which is thought to be due to zinc interstitials.[4] The increase of the longer wavelength absorption also for the 15 min sample at this fluence is an indication of scattering due to the presence of large particles in the product. In comparison to this, the 330 mJcm^{-2} samples display only a weak absorption peak at 300nm for 5min with very little long wavelength absorption at higher wavelengths for 15 min indicating the formation of very small particles via a more efficient reaction. The optical absorption spectra for samples prepared at 390 mJ cm^{-2} again indicate only a very weak absorption peak at 300 nm for 5min. However, a strong absorption for the longer wavelengths is prevalent at all growth times indicating the formation of large structures.

Due to the comparably small size of the laser assisted grown nanocrystals at 330 mJ cm^{-2} and the broadening of the size distribution observed at 170 and 390 mJ cm^{-2} laser fluences, the growth is considered to be governed by two factors: a size controlling

photothermal breakdown process and increased reaction rate due to laser irradiation. The hydrothermal growth of ZnO when $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and HMTA are used as the reactants is known to proceed through the following reactions:

The acceleration of the growth of ZnO nanocrystals is thought to occur through the absorption of the laser energy by $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ which then dissipates the heat to the surrounding resulting in an increase in the rate of reaction (1) which in turn accelerates reactions (2) and (3) in the forward direction. This rapid heating process will lead to the nucleation of a large number of ZnO units which over the period studied results in a defocused growth (Ostwald ripening) leading to the broad size distribution observed. The formation of smaller crystals compared to the reference is also attributed to the formation of large number nuclei for further growth. In comparison to this, the higher fluence of 330 mJ cm^{-2} can be thought of to lie in the window where photothermal breakdown effectively starts taking place with an effect that is almost equal to the OH^- formation rate. As a result, the nanocrystals that are formed attain a particle like morphology with a narrow size distribution. Increasing the fluence further would further increase the photothermal breakdown process, but also increases the rate of reactions (1) – (3). Domination of the reaction rates over the photothermal breakdown in this region would explain the formation of bi/tri/tetra-pod structures which are grown on nanocrystals seeds formed as a result of photothermal breakdown.

As nanocrystals possess a high surface area to volume ratio, these morphologies have been found to be of interest for applications such as gas sensors[5] and photo detectors.[6] Therefore a preliminary investigation on the electrical properties was carried out by drop casting the solution onto Au electrodes followed by annealing the films at 443 K to remove any excess water. The I-V characteristics of ZnO nanocrystal thin films prepared at 330 mJ cm^{-2} by 10 min laser irradiation is given in figure 4. An exponential behaviour is observed from the I-V characteristics of the ZnO thin film indicating that a Schottky type contact has been formed at the ZnO/Au interface as has been reported in the literature.[7] The conduction properties of the thin film itself with very little pre-treatment are seen to be poor with currents in the order of 10^{-8} A being achieved at $\sim \pm 15 \text{ V}$. Further work is underway to study and improve the electrical properties of these nanocrystals.

4. Conclusion

In conclusion, it has been shown that morphology and size controlled growth of ZnO nanocrystals can be achieved through UV laser irradiation of a traditional hydrothermal growth system. Evidence indicates the presence of a narrow fluence window around 330 mJ cm^{-2} in which nanoparticles can be formed with a narrow size distribution and little variation in mean size over the growth time. I-V characterization of a thin film of ZnO indicates that the material is a poor semiconductor forming a Schottky contact with Au.

Acknowledgement

The authors wish to thank the EPSRC (UK) for funding this work and the studentship awarded.

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figure 1 SEM images of the reference samples (laser fluence = 0 mJ cm⁻²) grown for a) 5 min and b) for 15 min. A change in morphology is evident with very little change in the length of the crystals.

figure 2 TEM images of ZnO nanocrystals grown using a fluence of (a) 170 mJ cm⁻² for 5 min, (b) 170 mJ cm⁻² for 5 min, (c) 330 mJ cm⁻² for 5 min, (d) 330 mJ cm⁻² for 12.5 min, (e) 390 mJ cm⁻² for 15 min. Figure f) displays the size distribution for ZnO nanocrystals grown at a 330 mJ cm⁻² laser fluence for 5 min.

figure 3 Absorbance spectra of ZnO nanocrystals grown at different fluences for different growth times. a) 5 min at 170 mJ cm⁻², b) 15 min at 170 mJ cm⁻², c) 5 min at 330 mJ cm⁻², d) 15 min at 330 mJ cm⁻², e) 5 min at 390 mJ cm⁻² and f) 15 min at 390 mJ cm⁻².

figure 4 I-V characteristics of ZnO nanocrystals prepared under 330 mJ cm⁻² laser for 10 min studied using an IDE structure with Au electrodes and finger spacing of 2.5 μm. The band alignment of ZnO and Au as well as the IDE structure used are also shown.

figure 1

figure 2

figure 3

figure 4