Laser-assisted hydrothermal growth of size-controlled ZnO nanorods for sensing applications.

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Abstract. Pulsed laser irradiation is used to seed the low-temperature hydrothermal growth of ZnO nanorods. UV laser irradiation produces ZnO nanoparticles in solution that act as nucleation seeds for the subsequent hydrothermal growth of the nanorods. By systematically varying the seed density and/or the concentration of the reactants, the diameter of the nanorods can be controlled over a wide range with a narrow size distribution. The nanorods are linked into multi-pod structures, due to nucleation at a central seed, but ultrasonic processing of the solutions is shown to yield isolated nanorods. Three dimensional networks of these multi-pod structures are fabricated by drop cating the solution onto interdigitated electrodes and gas sensors, operating at room temperature, for ethanol, and water vapour and UV photo-sensor devices are demonstrated.

1. Introduction

The properties of ZnO make it of great current commercial and scientific interest. ZnO has a wide direct band gap, which coupled with the large exciton binding energy (60 meV), makes it a candidate for a variety of optoelectronic device applications such as light emitting diodes, lasers and UV photo-detectors [1, 2]. ZnO gas sensors have also been demonstrated, with sensitivity to a range of vapours including alcohols, water vapour, ammonia and hydrogen [3, 4, 5, 6, 7, 8]. The sensing mechanism common to semiconducting metal oxides, such as ZnO which is typically n-type due to oxygen vacancies and/or interstitial Zinc, involves the formation of a charge depletion layer on the surface due to electron trapping at adsorbed oxygen species [9, 6]. Adsorption of reducing gas molecules leads to the release of electrons and thus an increase in the electrical conductivity.

The demand for high-sensitivity but low-cost environmental sensors that respond quickly to appropriate stimuli is growing rapidly. Macro scale components and conventional manufacturing techniques cannot provide sensors that deliver the detection levels and low temperature operation increasingly required for future applications. For example thin-film metal oxide based gas sensors typically require heating to 200-400°C. Hence, the move toward sensors fabricated from nanomaterials [10], such as metal oxide nanorods [3, 4, 5, 7, 8, 6] that offer lower temperature operation and high-sensitivities due, primarily, to their high surface area to volume ratios.

The synthesis of ZnO nanorod structures is carried out typically using chemical vapour deposition [11], vapour transport [12], or pulsed laser deposition techniques [13]. However, industrial processes increasingly require lower temperature techniques to allow device fabrication on low cost substrates such as plastics. Recently an economic, low temperature hydrothermal route for the production of ZnO micro and nanorods on a variety of substrates from aqueous solutions of Zn salts was developed [14, 15]. However, the dimensions of the ZnO nanorods structures fabricated using chemical methods are typically difficult to control when compared to nanorods prepared via vapor-phase methods. Methods to seed the substrates prior to growth have been demonstrated and have proved effective at giving some size control [16, 13]. Here, we introduce a technique that allows improved control over the size of the nanorods via photo-seeding prior to hydrothermal growth. Rather than growing nanorods on substrates, here the direct seeding occurs in solution, providing a route to grow size controlled ZnO nanorods that remain in solution for rapid subsequent device processing. This technique produces clusters (multi-pods) of size-controlled ZnO nanorods in solution, which we use to demonstrate the fabrication of vapour and UV photo-sensor devices by simple drop-casting.

2. Experimental methods

The initial ZnO nanoparticle solutions were synthesized by a UV irradiation technique, using the pulses from a Lambda-Physik LPX 210i excimer laser operating at 248 nm, with a pulse duration of 25 ns. 20 ml of an aqueous solution of Zinc Nitrate Hexahydrate and Hexamethylenetetramine (HMT) (3mM in both reactants) was placed in a vessel mounted on an X-Y translation stage. The reactants were heated before mixing and maintained at 90°C throughout the irradiation. Laser pulses with energies in the range 60-140 mJ were focused to produce a rectangular spot of with fluences in the range ~ 170 -390 mJ/cm². This laser spot was raster scanned over the whole area of the vessel for 10 minutes. A laser shot repetition rate of 40 Hz was used throughout the experiments.

Once the nanoparticle solutions were formed, they were used to deliver dispersed seed particulates to a separate vessel for the hydrothermal growth of ZnO nanorods. The hydrothermal synthesis was continued at 90°C for 12 hours. After synthesis, the reaction was terminated by plunging the vessel into cold water. To remove the remaining reactants, the solutions were centrifuged and the sedimented products separated from the liquid. The products were then re-dispersed in de-ionised water, where they would remain in solution for up to an hour.

The nanostructure of the products was investigated in a FEI Quanta 200 scanning electron microscope (SEM) and a Philips CM200 transmission electron microscope (TEM). The TEM was operated at 200 kV and was also used to obtain the crystal structure of the products by selected area electron diffraction (SAED). The optical absorption of the products was determined in a Cary 5000 UV-Vis-NIR spectrometer and their photoluminescence (PL) properties were measured using a Cary Eclipse fluorescence meter using 335 nm filtered excitation. Sensor devices were fabricated by drop-casting small volumes of the resulting nanorod solutions onto lithographically defined gold inter-digitated electrodes (spacing 5-20 μ m) on silicon dioxide substrates. The gas sensing response was determined by measuring the device resistance at constant current (using a Keitley 2400 sourcemeter controlled by a LabView program. Vapour exposure was controlled by placing the sensor device in a chamber with a constant through-flow of room air and introducing vapour at the air inlet. The chamber temperature and humidity were monitored continuously during the measurements. Photo-sensing response was measured again by changes in the sample resistance at constant current. UV light exposure was generated by the strongly attenuated pulses from a frequency-tripled Nd:YAG laser (5 ns pulses). The laser fluence was estimated as 40 μ J/cm².

3. Results and Discussion

3.1. Formation of ZnO seed particles

Figure 1(a) shows a TEM image of the nanoparticles produced by laser irradiation of the hydrothermal growth mixtures at a fluence of 330 mJ/cm². Inset in (a) is a SAED

pattern confirming that the nanoparticles assume the ZnO wurtzite crystal structure. The particles have a narrow size distribution, and on closer inspection are confirmed as single crystals. Figure 1(b) shows the optical absorption spectra of the nanoparticle solutions produced at laser fluences in the range 0- 390 mJ/cm². Without the laser exposure, there was no evidence of the strong UV absorption of the ZnO products, the weak absorption peak at ~ 300 nm is the absorption of the zinc nitrate and indeed, SEM analysis (not shown here) confirms that without the laser irradiation, only a very low density of low-aspect ratio, micron-sized, microrods grow during the 10 minute synthesis. As the laser fluence is increased from 170 mJ/cm² to 330 mJ/cm², the near-band-edge absorption of the ZnO increases - suggesting that the higher laser fluence produces more ZnO nanoparticles. However, at 390 mJ/cm² the absorption reduces, which may be a consequence of photo-induced degradation of the nanoparticles during the irradiation process. Here we suggest that the laser energy accelerates the initial stages of the hydrothermal reaction - similar acceleration has been observed when sonic power [17] or microwave exposure [18] is used. The first stage of the ZnO growth reaction involves the slow thermal decomposition of the HMT to release hydroxide ions. The localised laser heating via absorption in the zinc nitrate or direct photo splitting of water may accelerate this process, producing large numbers of hydroxide ions during the pulse. Rapid quenching after the pulse should result in the formation of a high density of nanoparticulates, rather than the growth of extended crystallites which occurs when the nucleation rate is slower. An extensive investigation of the growth of these seed particles was performed, but is beyond the scope of this paper.

3.2. Growth of ZnO nanorods

After the formation of the nanoparticles, these solutions were used to inject growth seeds into hydrothermal zinc nitrate/HMT mixtures in order to control the growth of ZnO nanorods. It was possible to simply allow the irradiated mixture to continue growing nanorods after the seeds were formed, but for a complete study of the growth mechanisms it was found to be more convenient, and give a higher yield, to deliver a controlled volume of known seed solution to a Zinc Nitrate/HMT mixture with different concentrations. Hence, hydrothermal growth mixtures with a range of concentrations of the reactants plus a known volume of the 330 mJ/cm² irradiated seed solution were used. Although the volume of the seed solution was varied, the actual volume of liquid introduced was kept constant by making up the remainder with distilled water. Table 1 summarises the different mixtures used. As both the concentration of the reactants and the volume of seed solution were varied, an arbitrary ratio R_{ZS} was defined to classify the mixture to aid subsequent analysis. The dimensionless ratio chosen was the volume of the zinc nitrate solution used to the volume of the seed solution added. As the total volume of the mixtures was kept constant at 10 ml, this ratio is representative of the amount of ZnO available per seed particle introduced. After the growth, the nanostructure of the products was examined in the SEM. Figures 2(a)–(h) are images

taken from samples (1)–(8), respectively. The nanorods grow in multi-pod structures, linked at a central point, which we suggest is a seed or cluster of seed particulates. It is clear that as R_{ZS} decreases from 16:1 to 0.5:1 the diameter and length of the nanorods decreases demonstrating that it is possible to control the morphology of the rods via varying the nucleation density and the supply of reactants. As the nanorod nucleation density is increased, the amount of reactants available per nuclei decreases, and hence the nanorods are smaller. To further examine the nanorod morphology the samples were examined in the TEM. Figure 3(a) shows a TEM image of ZnO nanorods grown for a seeded hydrothermal mixture with $R_{ZS}=1:1$. The nanorods appear with a well-formed morphology and are confirmed as single crystals by selected area electron diffraction.

Although, in the concentration range examined, the R_{ZS} value appears to be the controlling parameter to determine the nanorod diameter, it was important to determine if this seeding mechanism was valid over a wider range of concentrations. To test this, a hydrothermal mixture with a R_{ZS} value of 24:1 was used using 4 ml of 75 mM of the each of the reactants, 1 ml of the seed solution and 1.5 ml of water. A SEM image of the products is shown in figure 3(b). From this image, it can be observed that the direct correspondence between the nanorods diameter and R_{ZS} no longer holds. There is a much wider distribution of nanorod diameters for this sample. It is suggested that when the reactants are at a great excess with respect to the seed particles, the nucleation of nanorod growth does not only occur at the seeds. Spontaneous nucleation in the solution is also occurring. This idea is supported by the observation that, for mixtures with $R_{ZS} > 16:1$, the glass reaction vessel and any substrate placed in the mixture is also covered by ZnO nanorods. This did not occur for $R_{ZS} < 16:1$ where growth only occurred in solution. The results here indicate that the change in morphology occurs somewhere between $R_{ZS} = 16:1$ and $R_{ZS} < 24:1$.

Figure 4(a) shows a plot of the mean nanorod diameter as a function of R_{ZS} . If the number of nanorods per multi-pod and the aspect ratio of the nanorods both remained constant, an cube-root dependence of the diameter on R_{ZS} would be expected. However, from figure 4(a) a linear or slightly super-linear dependence is observed, suggesting that that these values are not constant. The slightly super-linear dependence could be an indication of the onset of the decoupling of rod size from the seed density when the reactant concentration is high, as discussed earlier. From figure 2 it appears that as R_{ZS} increases there are fewer nanorods per multi-pod and the aspect ratio of the nanorods decreases.

Having demonstrated control of the morphology, it is important to determine the effect of the nanostructure on the optical properties of the multi-pods. Figure 4(b) shows the PL spectra of solutions of the multi-pods. Note that the sharp feature at 470 nm is due to fluorescence from one of the filters used, and can be ignored. From this figure, it can be seen that as the size of the nanorods decreases a blue-shift in the near-band-edge UV luminescence from 390 nm to 381 nm occurs, as has been observed by other groups [19, 20]. The nanorods are too large for this to be attributed to a quantum confinement effect, as the diameter is significantly larger than the Bohr radius,

so this is likely attributed to surface effects, which are more important for smaller rods, or to variation in the lattice strain. Although it is clear that the surface effects and the depletion region caused by surface band bending are important to the PL of ZnO, the mechanism how the surface effects influence the PL is still debatable. All the samples show also a broad visible PL emission band centered at 580 nm. This band, attributed typically to point defects [21], is less intense than the UV emission for all the samples studied, indicating that the nanorods are relatively free of point defects. The ratio of the UV emission to the visible band does not change significantly with the size of the nanorods.

3.3. Sensor measurements

Having characterised the samples, the suitability of these materials for sensing applications was assessed. Drops of the solutions were delivered onto gold inter-digitated electrodes. Inset in figure 5 is optical microscope image of sample 5 deposited onto electrodes with a 20 μm spacing. Closer inspection of the devices shows that the multi-pod structures interlace with each other, as can be seen in figure 2, forming three dimensional networks. For nanorods with diameters significantly larger than the depth of the surface depletion layer, as is the case here, the resistance of the networks is determined by the potential barrier at the contacts between the rods [22]. The size of this barrier is strongly dependent on the extent of surface depletion of the nanorods [23], which can be modified by gas exposure. The aim here was to extract the nanorod size-dependence of the sensor response. However, producing devices with repeatable parameters proved difficult. The precise morphology of the three dimensional networks that formed after drying was random and the network resistances could vary by an order of magnitude even when using the same source solution. Hence, it was impossible to disentangle the size dependent factors from the stochastic error. Thus the response of a single device to a range of parameters was examined in order to investigate the potential of the material system.

ZnO gas-sensor devices have been reported in the literature on many occasions. However, the issue of cross-sensitivity and interference from environmental species such as water vapour are generally overlooked. In order to function adequately in ambient conditions gas sensors need to be tolerant to natural variations in the ambient relative humidity (RH). Figure 5 shows current-voltage curves for ZnO multi-pod sample 5 for different relative humidities (RH). The diode-like shape of the curves indicate that ZnO forms a Schottky contact with the gold. The ZnO-gold interface is expected to form a Schottky contact [24] with a barrier of nearly 1 eV. The samples show a dramatic, reversible, increase in current as the RH is increased, for all voltages above the Schottky barrier. At an applied voltage of 1.8 V, the increase in current is nearly two orders of magnitude for variations in RH from 25% to 72% - a range similar to that observed in outdoor ambient air. This indicates that any environmental sensor based on these materials would have to be compensated to adjust for these variations - a factor that

is often overlooked in the literature when discussing sensitivities. Despite this strong interference, the suitability of these samples for detecting other analytes was assessed. Here we present the response of sample 5 to 20 second exposures of ethanol vapour in flowing ambient air at a fixed RH of 41%. It is important to note that the device was operated at room temperature, rather than the 200-300°C that is used typically for metal oxide sensor devices. Figure 6 shows the response of the device (defined as the % change in the device resistance upon exposure.) The precise exposure level was not measured in this simplistic test, but it is encouraging to observe a significant repeatable response for room temperature operation. The recovery time of the device was around 10 minutes, a value that would be expected to improve if substrate heating were used. Further, more accurate, response measurements are planned.

As a final assessment of the potential of these materials, the modification of the conductivity on UV exposure was evaluated. This property is important to assess for optoelectronic applications such as UV photosensors as ZnO nanorods have been shown to exhibit persistent photoconductivity due to trapping of charge carriers by oxygen vacancies [25]. This photo-conductivity also needs assessment for applications of these materials as environmental sensors, where the sensor is exposed to ambient light levels. To investigate the photoconductivity in these materials, a device made from sample 5 was exposed to UV laser pulses at a repetition rate of 20 Hz. On exposure the conductivity of the sample increased and the laser exposure was continued for 1000 shots, until the change in conductivity had begun to saturate. A plot of the device response is shown in figure 7. After exposure, the recovery to the dark-conductivity level fitted well to an exponential decay function and persisted with a decay constant of 10.4 minutes, a similar value to that reported elsewhere [25]. We suggest that this persistent photoconductivity is due to charge trapping at defect states, as photo-induced desorption of water or oxygen molecules by the laser pulses would be expected to decrease, rather than increase, the conductivity. It should be noted that no transient direct photo-current, immediately after the laser pulse, was observed for these samples.

As shown previously, the nanorods produced are linked together into multipod structures. However for many applications, such as individual nanowire transistors, this morphology may not be ideal. Hence, techniques to break up the multipods into individual nanorods were investigated. Figure 8 shows a multipod sample (a) before and (b) after exposure to a 750 W, 20 kHz ultrasonic probe running at 40% of maximum output for 3 minutes. It can be clearly observed that the multipods are broken up into individual nanorods with lengths similar to that in the starting solution. This suggests that the weakest point in the multipod structure is the central link and that this can be broken with little damage to the individual rods.

4. Conclusions

In conclusion, we have demonstrated that pulsed laser irradiation of ZnO hydrothermal growth mixtures is an effective way to seed the growth of nanorods in solution.

By varying the ratio between the reactant concentration and the number of seed nanoparticles it was possible to control the size of the resulting nanorods over a wide range. The nanorods produced are linked together in multi-pod structures, likely due to nucleation at a central seed, but can be broken up into individual nanorods by ultrasonic treatment. An ethanol sensing device is demonstrated based around the multipod structures, operating at room temperature. It is suggested that the resistance of these three dimensional networks of multipods is contact-controlled. By varying the ambient humidity and by exposure to UV light, we show that these devices have a strong interference with other environmental parameters, limiting possible application as a sensor unless these can be overcome.

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Tables

Table 1. Details of the hydrothermal mixtures used to grow the ZnO nanorod samples. The ratio of the volume of the zinc nitrate to the volume of the seed solution was used to define the arbitrary ratio in the last ratio column.

Sample	Zinc Nitrate conc./volume	HMT conc./volume	Seed solution volume	Water volume	Ratio Reactants:Seed (arb.units)
Sample 1	25mM, 0.5ml	25mM, 0.5 ml	1ml	8ml	0.5:1
Sample 2	25mM, 1ml	25mM, 1ml	1ml	7ml	1:1
Sample 3	25mM, 2ml	25mM, 2ml	1ml	5ml	2:1
Sample 4	25mM, 3ml	25mM, 3ml	1ml	3ml	3:1
Sample 5	25mM, 4ml	25mM, 4ml	2ml	0ml	2:1
Sample 6	25mM, 4ml	25mM, 4ml	1ml	1ml	4:1
Sample 7	25mM, 4ml	25mM, 4ml	0.5ml	1.5ml	8:1
Sample 8	25mM, 4ml	25mM, 4ml	0.25ml	1.75ml	16:1

Figure 1. (a) TEM image of the ZnO nanoparticles produced by laser irradiation at 330 mJ/cm². Inset in (a) is a SAED pattern confirming the wurtzite crystal structure. (b) Optical absorption spectra of the nanoparticle solutions produced at laser fluences of (i) 0 mJ/cm², (ii) 170 mJ/cm², (iii) 330 mJ/cm², and (iv) 390 mJ/cm².

Figure 2. SEM images of the ZnO nanorods grown after injection of seed particles into the hydrothermal mixture. Images (a)–(h) are taken from sample (1)–(8), respectively.

Figure 3. (a) TEM image of ZnO nanorods grown for a seeded hydrothermal mixture with $R_{ZC}=1:1$ (b) SEM image of the nanorods produced with a seeded hydrothermal mixture with $R_{ZC}=24:1$

Figure 4. (a) Dependence of the mean nanorod diameter on the ratio R_{ZS} . (b) Photoluminescence spectra for (i) Sample 1, (ii) Sample 2, (iii) Sample 3, (iv) Sample 4, and (v) Sample 6. As the size of the nanorods decreases a blue-shift in the near-band-edge luminescence is observed, as indicated by the dashed guide line.

Figure 5. Current-voltage curves for ZnO multi-pod sample 5 for different relative humidities (RH). Inset is an optical microscope image of the sample deposited onto interdigitated electrodes.

Figure 6. Electrical response of sample 5 to 20 second exposures of ethanol vapour in flowing ambient at air at a fixed RH of 41%. Ethanol exposure was started at points a, c, e, and g and stopped at points b, d, f, and h.

Figure 7. Photo-sensing response for multi-pod sample 5, measured by changes in the sample resistance at constant current.

Figure 8. SEM images of a multipod sample (a) before and (b) after exposure to an 750 W, 20 kHz ultrasonic probe running at 40% of maximum output for 3 minutes.