Nanotechnology **19** (2008) 255608 (5pp) doi:10.1088/0957-4484/19/25/255608

Rapid synthesis of aligned zinc oxide nanowires

Husnu Emrah Unalan[1], Pritesh Hiralal, Nalin Rupesinghe, Sharvari Dalal, William I Milne and Gehan A J Amaratunga

Electrical Engineering Division, Department of Engineering, University of Cambridge, 9 J J Thomson Avenue, Cambridge CB3 0FA, UK

E-mail: heu22@cam.ac.uk

Received 5 February 2008, in final form 21 April 2008
Published 15 May 2008
Online at stacks.iop.org/Nano/19/255608

Abstract

A solution growth approach for zinc oxide (ZnO) nanowires is highly appealing because of the low growth temperature and possibility for large area synthesis. Reported reaction times for ZnO nanowire synthesis, however, are long, spanning from several hours to days. In this work, we report on the rapid synthesis of ZnO nanowires on various substrates (such as poly(ethylene terephthalate) (PET), silicon and glass) using a commercially available microwave oven. The average growth rate of our nanowires is determined to be as high as 100 nm min^{-1}, depending on the microwave power. Transmission electron microscopy analysis revealed a defect-free single-crystalline lattice of the nanowires. A detailed analysis of the growth characteristics of ZnO nanowires as functions of growth time and microwave power is reported. Our work demonstrates the possibility of a fast synthesis route using microwave heating for nanomaterials synthesis.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, semiconducting nanowires have attracted much attention due to their unique optoelectronic properties [1–3]. Among semiconducting oxide nanowires, ZnO is one of the most promising materials with its direct wide bandgap and large exciton binding energy. Applications such as UV nanolasers [4], field effect transistors [5], solar cell electrodes [6] and nanogenerators [7] utilizing ZnO nanowires have been reported. Common ZnO nanowire synthesis methods include gas condensation using catalytic reactions [8–10] and the hydrothermal methods [11, 12]. It is possible to synthesize highly crystalline and high aspect ratio ZnO nanowires using gas phase approaches; however, high synthesis temperatures and vacuum requirements limit large scaling of the substrate and, consequently, device integration. The hydrothermal method, on the other hand, can produce ZnO nanowires at low temperatures and atmospheric pressure over large areas on any type of substrate. Due to its versatility and simplicity, the hydrothermal ZnO nanowire synthesis method has been investigated by many researchers. It has been shown that it is possible to grow perfectly aligned ZnO nanowires [13]. In that work, ZnO nanocrystals were used as seed layers which are obtained by spin coating zinc acetate solution in ethanol followed by a thermal treatment. Control of the size and position of the nanowires was achieved by the use of a patterned substrate [14]. A problem associated with hydrothermal synthesis is the time required for the synthesis of nanowires spanning from several hours to days [6]. Recently, tip sonication was investigated as a quick route for the aligned ZnO nanowire synthesis and average growth rates of 500 nm h^{-1} has been reported [15]. However, there is a need to develop techniques for rapid, large area growth of ZnO nanowires.

Microwaves have been extensively used for rapid heating of materials e.g. carbon nanotubes functionalization [16] and annealing of organic photovoltaic devices [17]. Microwave energy transforms into heat inside the material which reduces the energy consumption, decreases the process time and provides rapid and controllable volumetric heating with a particular temperature distribution. Due to the shorter residence times, higher purity products can be achieved. Microwave heating has been investigated for rapid synthesis of micron sized ZnO particles by Hu *et al*, however, growth of ZnO nanowires on substrates has not yet been achieved [18].

[1] Author to whom any correspondence should be addressed.

2. Experimental details

Here we report on the use of microwave heating for the rapid, hydrothermal synthesis of aligned ZnO nanowires on various substrates. ZnO nanowires were grown hydrothermally based on the method developed by Greene *et al* [11, 13]. Specifically, a 10 mM solution of zinc acetate dihydrate (98%, Aldrich) and 1-propanol (spectroscopic grade) was prepared. The solution was then spin coated on n-type silicon [(100), $R = 0.015$–$0.025\ \Omega$ cm], glass and poly(ethylene terephthalate) (PET) substrates at 2000 rpm for 30 s. Prior to spin coating, the substrates were cleaned by sonication in acetone and isopropanol for 10 min and dried in a nitrogen flow. The substrates were then annealed at 100 °C for 1 min after each spin coating to enhance adhesion. A uniform seed layer was obtained after three layers of spin coating. Vertical ZnO nanowires were then grown by dipping the substrates in a mixture of equimolar 25 mM zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, Sigma Aldrich) and hexamethylenetetramine (HMTA, Sigma Aldrich) solution in deionized (DI) water (resistivity 16 MΩ cm) and heating with a commercially available microwave oven (2.45 GHz) at different power settings (120, 385 and 700 W) at atmospheric pressure. A turntable inside the microwave revolved at 4 rev min^{-1} to ensure homogeneous heating of the solution. For comparison purposes, several samples were grown at 90 °C using a furnace. Microwave heating was performed for 1–30 min. The substrates were then removed from the growth solution, rinsed with DI water and dried under nitrogen flow. The morphology and size of the ZnO nanowires were investigated by field emission scanning electron microscopy (FESEM) (JEOL 6340F, operated at 5 kV) and the crystallinity of the ZnO nanowires was investigated using high resolution transmission electron microscopy (HRTEM) (JEOL 3011 operated at 300 kV). HRTEM samples were prepared by scraping wires off the substrates, followed by dispersion in methanol and then drop cast onto holey carbon coated copper grids. The crystal structure of the ZnO nanowires was observed using x-ray diffraction (XRD) using a Philips PW1730 diffractometer with Cu Kα radiation. The optical characteristics of the as-grown nanowires were investigated using photoluminescence (PL) and absorption measurements. The PL measurements were performed at room temperature with the 266 nm line of an Nd:YAG laser. Optical absorption measurements were made using a Thermoelectron Corporation UV/VIS Spectrometer UV2 double beam spectrophotometer.

3. Results and discussion

FESEM images of the ZnO nanowire arrays grown at a microwave power of 700 W for 3 min on silicon, glass and PET substrates are shown in figures 1(a)–(c), respectively. It can be seen that the ZnO nanowires have tapered tips and were vertically aligned on all of the substrates. The hexagon shaped morphology of the as-grown nanowires could be clearly observed in the top view SEM images (inset). Cross sectional SEM images revealed that the length of the ZnO nanowires

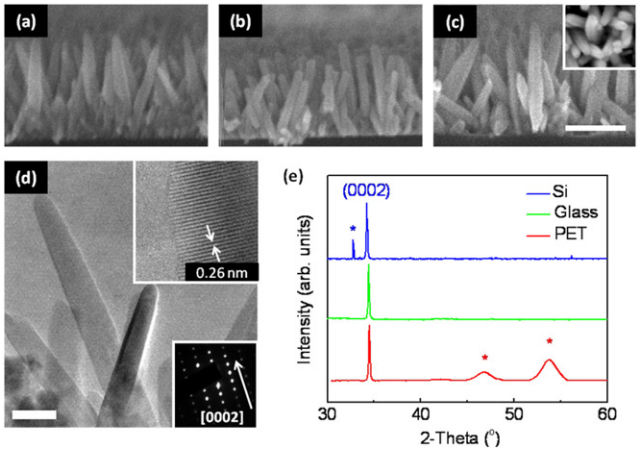

Figure 1. SEM image of ZnO nanowire arrays grown on (a) Si, (b) glass and (c) PET substrates. Inset shows top view of the array. Scale mark 200 nm. (d) TEM image of the nanowire array on Si. Scale mark 50 nm. Inset shows HRTEM image and corresponding electron diffraction pattern. (e) XRD patterns of ZnO nanowires grown on different substrates. Peaks from the substrates were marked with an asterisk.

can be controlled by adjusting the microwave power and the growth time. The growth rate of ZnO nanowires by microwave heating is ∼75–100 nm min^{-1}, much higher than found in other hydrothermal approaches.

Further structural analysis was performed using TEM. Figure 1(d) shows TEM image of ZnO nanowires grown on Si substrates. A selected area electron diffraction (SAED) pattern of a single nanowire (inset) shows that the nanowires are single crystalline and grow in the [0001] direction, *c*-axis of the ZnO crystal lattice. In addition, the lattice spacing of 0.26 nm obtained from high resolution images, matches the interlayer spacing of the (0002) planes in the ZnO crystal lattice. TEM analysis from ZnO nanowires grown by microwave heating on Si, glass and PET substrates yielded similar results confirming the [0001] growth direction. Detailed TEM analysis did not reveal any structural damage such as stacking faults or dislocations in the microwave grown nanowires. XRD spectra from nanowires grown by microwave heating on various substrates are shown in figure 1(e). These can be compared with XRD spectra for nanowires grown by furnace heating. ZnO nanowires grown with microwave and furnace heating both revealed a strong peak around 34.8° corresponding to the (0002) spacing of the wurtzite structure of ZnO, indicating the preferential alignment in *c*-axis direction.

Figure 2(a) compares the PL spectra of ZnO nanowires of similar length grown using microwave heating and furnace heating. Both nanowire arrays show a strong free exciton emission at 3.29 eV and a weak, broad deep level emission centered at 2.03 eV. Excitonic PL emission shows a small FWHM value of about 140 meV for microwave and furnace grown samples indicating that the optical quality of the microwave grown samples are comparable to the furnace grown ones. The intensity of the defect related band was found to increase with microwave heating time, however, it was still lower than that of the furnace grown samples. Long

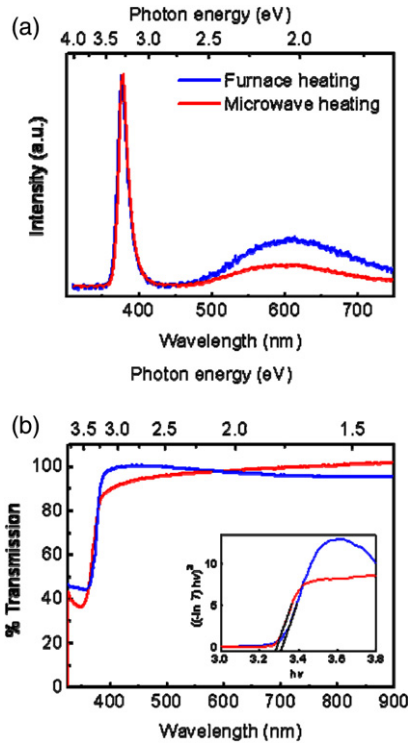

Figure 2. PL spectrum (a) and optical transmission spectrum (b) of furnace and microwave grown ZnO nanowire arrays. Inset shows plot of $(\alpha h\nu)^2$ versus energy curves for the samples.

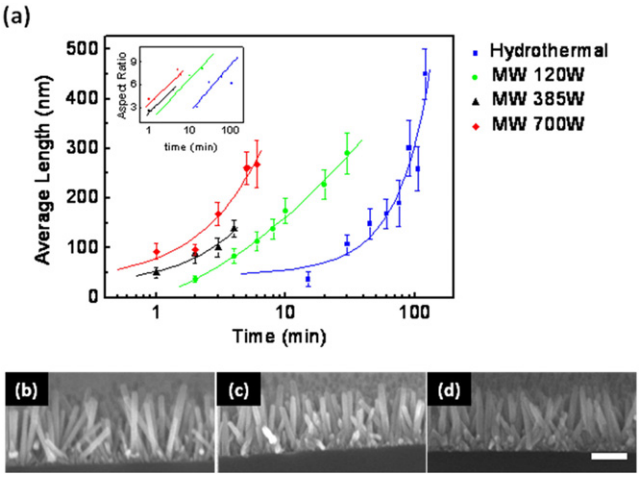

Figure 3. (a) Axial growth rates of samples at different microwave powers as compared to hydrothermal growth with standard deviation. Polynomial fits were shown for visualization. Inset shows the aspect ratio of the same samples. SEM images of ZnO nanowire arrays grown in (a) furnace for 90 min, (b) microwave at 120 W for 30 min and (c) microwave at 700 W for 6 min. Scale mark 200 nm.

wavelength emission band could be attributed to the lattice defects. It is known that after some time in the growth solution, ZnO nanowires slowly redissolves which may result in defects. Our microwave process simply reduces the time available for this dissolution to occur, leading to less defects compared to furnace growth. The normal incidence transmittance of our ZnO nanowire arrays in the 1.5–4 eV photon energy range is shown in figure 2(b). Nanowires exhibit good transparency in the visible range and a sharp absorption onset around 360–380 nm for both microwave and furnace grown samples. This is attributed to the good crystallinity and the reduced number of defects in the nanowires. The bandgap of the microwave and furnace grown ZnO nanowires were estimated to be 3.284 and 3.309 eV, respectively, from a linear fit of $(\alpha h\nu)^2$ versus energy $(h\nu)$ plot, as suggested by Anthony *et al* assuming a direct band gap [19]. α, the absorption coefficient, is assumed to be proportional to $-\ln T$, where T stands for the transmittance of the arrays. Thus, microwave heating shortens the growth time without altering the structure and optical properties of the nanowires.

Axial (length) growth rates of samples produced at different microwave powers are shown in figure 3(a). Lengths of furnace grown wires are included for comparison. For calculation of the nanowire dimensions, cross sectional SEM images have been used and processed using ImageJ image processing software. Dimensions were averaged from 100 individual nanowires. Aspect ratios of the ZnO nanowires are shown in the inset. As with furnace heating, microwave heating was found to enhance both the axial and lateral growth rates of the nanowires where the former was found to be a lot quicker than the later. The aspect ratios of the nanowires with similar lengths grown at different power levels or in the furnace yielded similar values. The microwave power level was found to be proportional to the growth rate of the nanowires. The effect of microwave growth can be observed even at low microwave powers (120 W) as compared to furnace heating. This can be attributed to the rapid heating of the reaction precursors to the crystallization temperature and, the shorter crystallization times associated with the rapid dissolution of precipitated hydroxides by the microwave heating. Therefore, longer nanowires are obtained at higher microwave power levels. Samples grown at high microwave powers (700 W) revealed growth rates 15 times faster than the hydrothermal growth rates in our control experiments. Cross sectional SEM images of the ZnO nanowire arrays with the same length that are grown in the furnace for 90 min, microwave at 120 W for 30 min and at 700 W for 6 min are shown in figures 3(b)–(d), respectively. The effect of microwave heating and power on enhancing the aspect ratio can be clearly seen.

Water has a high dipole moment that makes it a good solvent for microwave assisted reactions. In order to prove that only water is heated in our experiments, substrate temperatures were measured at different microwave power levels for the growth times indicated before. Liquid temperature lacquers (Omegalaq) were used for *in situ* monitoring substrate temperature in microwave heating. Lacquers liquefy and change appearance when a target temperature is reached. Substrates with applied temperature lacquers were then exposed to microwave heating. No change in the lacquer appearance was observed for the indicated power levels and times. Therefore, substrate heating effects can be excluded in our experiments. Heating of water above its normal boiling point, i.e. superheating, is possible by microwave heating. Superheating occurs in the absence of nucleation centers for

the vapor phase, i.e. bubbles. However, this can be avoided by introducing a rough surface, such as Teflon substrate holders used in our experiments. Thus, we can exclude superheating and the temperature is limited by the evaporation of water at its boiling point. During nanowire growth, substrates were repeatedly introduced to fresh solution baths in order to obtain long wire arrays. Microwave irradiation has been widely used for the sintering of ceramic materials which would cause thin film formation rather than nanowires. However, ZnO has been reported to be 'difficult to heat' with microwave irradiation, having an approximate heating rate of 25 °C min^{-1} [20]. Therefore, detailed TEM analysis did not reveal any structural damage or sintering for the growth times indicated in our experiments. Optical absorption spectroscopy and PL measurements confirmed the high quality of the microwave grown nanowires. Confirming that microwave heating can be used for the rapid synthesis of high quality ZnO nanowires.

We have found that, it is also possible to use this method for the growth of ZnO nanowires over large areas. In our control experiments uniform nanowire growth was achieved on a 4 inch silicon wafer. An optical image of the silicon wafer and SEM images of the ZnO nanowires are shown in figure 4. Top view SEM images were taken from the areas indicated with the arrows. In addition, we have successfully demonstrated the patterning of our ZnO nanowire arrays. Negative photoresist (*SU*-8 2) was used for patterning which was compatible with our seed solution. The thickness of the photoresist resist was ∼1.5 μm and it was soft baked at 90 °C for 1 min. The patterned substrates were then treated with oxygen plasma for 30 s in order to yield a hydrophilic surface. The catalyst seed solution was then spin coated and nanowires were grown at 700 W for 3 min in a microwave. Finally, photoresist was removed by microposit remover 1165 in a 60 °C bath. The photoresist did not show any damage during the microwave heating and upon removal did not leave any residue. The right-hand side inset in figure 4 shows an SEM image of patterned ZnO nanowires grown on the silicon substrates.

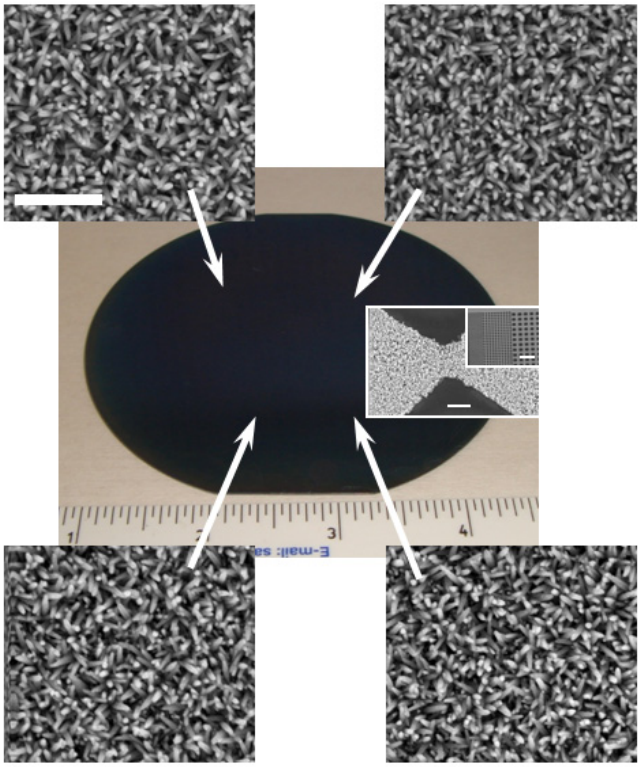

Figure 4. Image of a 4 inch Si wafer with ZnO nanowires grown by microwave heating. Insets: top view SEM images of ZnO nanowires on the Si wafer. The arrows point to the locations where the images were taken. Scale bar is 500 nm and corresponds to all 4 insets. Right-hand side inset shows the SEM image of patterned ZnO nanowire arrays on Si wafer. Scale bars for large and small insets are 1 μm and 100 μm, respectively.

4. Conclusions

In summary, we have demonstrated a rapid method to synthesize large area, vertically aligned ZnO nanowires on various substrates using microwave heating. High quality and less defective ZnO nanowires were synthesized in few minutes depending on the microwave power level and reaction times. This method of growth of ZnO nanowires could be used in large area applications ranging from light emitting diodes to antireflection coatings. Our work illustrates the feasibility of a simple and rapid microwave heating method which can be applied to a variety of other nanomaterial synthesis processes as well.

Acknowledgments

This work was partly supported by the Samsung Advanced Institute of Technology under the Advanced Nanomaterials for Electronics collaboration with the Cambridge University Engineering Dept.

References

[1] Duan X F, Huang Y, Cui Y, Wang J F and Lieber C M 2001 *Nature* **409** 66
[2] Duan X F, Huang Y, Agarwal R and Lieber C M 2003 *Nature* **421** 241
[3] Li Y, Qian F, Xiang J and Lieber C M 2006 *Mater. Today* **9** 18
[4] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897
[5] Cha S N, Yang J E, Choi Y, Amaratunga G A J, Ho G W, Welland M E, Hasko D G, Kang D-J and Kim J M 2006 *Appl. Phys. Lett.* **89** 263102
[6] Law M, Greene L E, Johnson J C, Saykally R and Yang P D 2005 *Nat. Mater.* **4** 455
[7] Wang Z L and Song J 2007 *Science* **312** 242
[8] Park W I, Yi G C, Kim M Y and Pennycook S J 2002 *Adv. Mater.* **14** 1841
[9] Wu J J and Liu S C 2002 *Adv. Mater.* **14** 215
[10] Yang P, Yan H Q, Mao S, Russo R, Johnson J, Saykally R, Morris N, Pham J, He R R and Choi H J 2002 *Adv. Funct. Mater.* **12** 323
[11] Greene L E, Law M, Goldberger J, Kim F, Johnson J C, Zhang Y, Saykally R J and Yang P D 2003 *Angew. Chem. Int. Edn* **42** 3031
[12] Greene L E, Yuhas B D, Law M, Zitoun D and Yang P 2006 *Inorg. Chem.* **45** 7535

[13] Greene L E, Law M, Tan D H, Montano M, Goldberger J, Somorjai G and Yang P 2005 *Nano Lett.* **5** 1231
[14] Kim Y-J, Lee A-H, Hong Y J, Yi G-C, Kim S S and Cheong H 2006 *Appl. Phys. Lett.* **89** 163128
[15] Jung S-H, Oh E, Lee K-H, Park W and Jeong S-H 2007 *Adv. Mater.* **19** 749
[16] Wang Y, Iqbal Z and Mitra S 2006 *J. Am. Chem. Soc.* **128** 95
[17] Ko C-J, Lin Y-K and Chen F-C 2007 *Adv. Mater.* **19** 3520
[18] Hu X L, Zhu Y J and Wang S W 2004 *Mater. Chem. Phys.* **88** 421
[19] Anthony S P, Lee J I and Kim J K 2007 *Appl. Phys. Lett.* **90** 103107
[20] Haque K E 1999 *Int. J. Miner. Process.* **57** 1