Controllable growth of vertically aligned zinc oxide nanowires using vapour deposition

S H Dalal[1], **D L Baptista**[1,4], **K B K Teo**[1], **R G Lacerda**[2],
D A Jefferson[3] **and W I Milne**[1]

[1] Electrical Engineering Division, Department of Engineering, University of Cambridge,
9 JJ Thomson Avenue, Cambridge CB3 0FA, UK
[2] Dept. de Física, Universidade Federal de Minas Gerais, 30123-970 Belo Horizonte, Brazil
[3] Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, UK

E-mail: shd21@eng.cam.ac.uk and dalbap@if.ufrgs.br

Abstract
The controllable growth of vertically aligned ZnO nanowires using a simple
vapour deposition method system is reported. The growth properties are
studied as a function of the thickness of the Au catalyst layer, total pressure,
deposition temperature and oxygen partial pressure. The experiments
indicate the existence of five main zones of growth. The zone in which the
aligned wires grow varies according to the pressure, temperature and oxygen
partial pressure. A specific level of low supersaturation of Zn and oxygen
vapour are both necessary to ensure the correct rate of growth, which then
leads to having thin and densely aligned wires. The growth kinetics are
discussed in terms of the interdependent variables. It was found that the
diameter and density of the nanowires is controlled mostly by the growth
temperature and pressure. The zone with the most aligned nanowires with the
highest aspect ratio was found to be at 5 mbar in a temperature range of
860–800 °C with a flow of 27 sccm of a N_2/O_2 mixture.

1. Introduction

ZnO, a direct wide band gap semiconductor ($\sim$3.3 eV), is the
focus of much research for its potential in fabricating light
emitting diodes [1], sensors [2] and UV laser diodes [3] due to
its large exciton binding energy ($\sim$60 meV) which is more than
two times higher than the thermal energy at room temperature.
It also has use as a piezoelectric [4] and transparent conducting
material [5], and potential as a diluted magnetic semiconductor
(DMS) [6].

A wide variety of ZnO nanostructures have been grown,
such as nanowires [7, 8], nanobelts [9], tetrapods [10],
nanorings [11] and nanocombs [12]. ZnO nanostructures
can have a modified density of states concentrated at certain

energy levels enabling greater light emitting efficiency [13].
Nanowires and nanorods, in particular, have been obtained
using techniques such as thermal evaporation [14], chemical
vapour deposition [15] and metal organic vapour phase
epitaxy [16]. Being able to control the diameter and length of
the nanowires is integral to many applications. By vaporizing a
mixture of ZnO and graphite one can deposit vertically aligned
nanowires onto lattice matched substrates [17]. The most
important parameters for creating aligned nanowire arrays are
the deposition temperature and pressure as well as the partial
pressure of oxygen in the chamber.

Our understanding of the growth parameters responsible
for growing aligned wires is still unclear. The kinetics of
the reactions during carbothermal reduction and reoxidation
of Zn vapour which leads to the formation of ZnO nanowires
is complex and involves many interdependent variables [18].
Although many papers suggest that the temperature defines

[4] Present address: Instituto de Física, UFRGS, 91501-970 Porto Alegre,
Brazil.

the conditions for growing aligned wires, the type of growth is also controlled by the pressure, oxygen availability and gas flow, which all affect one another and create a specific vapour environment which leads to alignment of the wires. Therefore, a general understanding of the conditions that control the growth is crucial for achieving reproducibility in vertically aligned growth. This is essential for actual applications involving ZnO nanowires.

In this paper we report the controlled growth of vertically aligned nanowires using a physical vapour deposition process with Au as the catalyst and a gas mixture of nitrogen and oxygen. In order to identify the growth conditions that form well-aligned nanowires we have performed a study of the effects of the various parameters that affect the growth. Specifically, we investigated the effects of catalyst layer thickness, the deposition temperature, total pressure and the oxygen partial pressure on the diameter, density and structure of the nanowires. The identification of five distinct zones of growth was observed using a phase diagram of pressure and temperature. After growth the wires were characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HREM) and x-ray diffraction (XRD). The best conditions for aligned growth and its relation to the reaction kinetics are discussed.

2. Experimental details

In the experiments, an *a*-plane sapphire substrate was cleaned using a solution of Hellmanex and then annealed in a furnace at 1000 °C to remove any defects. A thin layer of Au (1–10 nm) was then deposited on the clean sapphire substrates using a thermal evaporator.

After the Au catalyst layer had been deposited, the coated substrates were placed in a small quartz boat, which was then transferred to a quartz tube inside a horizontal tube furnace. ZnO and graphite powders were mixed in a 1:1 ratio by weight, placed in a quartz boat and put in the centre of the furnace. The Au-coated substrates were placed in a separate quartz boat further downstream (and at a lower temperature range 620–890 °C) from the powder mixture. The tube was then pumped down to a base pressure of 10^{-2} mbar using a rotary pump. A purified gas mixture which contained 21% oxygen in nitrogen was then flowed into the chamber, raising the chamber pressure to between 3×10^{-1} and 6×10^{-1} mbar, corresponding to gas flows between 17 and 42 sccm. The deposition pressure was set to between 1 and 9 mbar. The furnace was heated at $60°$ min^{-1} and the substrate was then left to anneal for 30 min. After the deposition, during cooling, the airflow direction and pumping direction were reversed to prevent any growth at other temperatures. After the reaction the substrate surfaces appeared to be light blue in colour.

SEM studies were performed on the substrates using a JEOL 6340F FEGSEM operated at 5 kV. HREM was performed on a JEOL 3011 operated at 300 kV. The HREM samples were prepared by scraping the nanowires off of the substrates and then dispersing them in an isopropanol ultrasonic bath and placing them onto holey carbon grids.
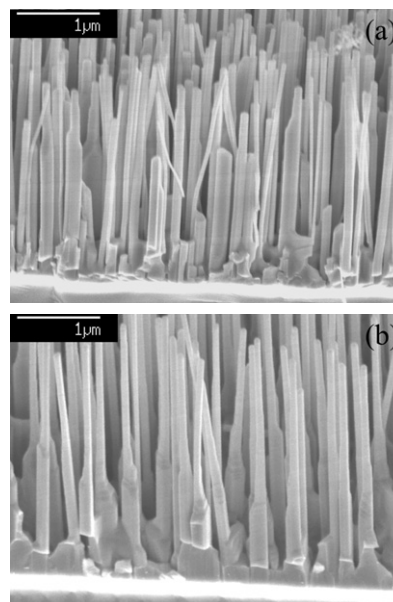
Figure 1. Vertically well-aligned ZnO nanowires grown on 1 nm (a) and 10 nm (b) Au-coated sapphire substrate at 3 mbar pressure and a temperature of 820 °C, using 27 sccm of purified air. Changes in vapour concentration may be causing the step-like changes in diameter.

3. Results and discussion

3.1. Influence of catalyst layer thickness

The thickness of the catalyst layer affects the diameter of the nanowires as well as the areal density. Figures 1(a) and (b) show SEM micrographs of two well-aligned ZnO nanowire samples grown using the same gas flow, pressure and substrate temperature but with different catalyst film thickness. Both samples show a very homogeneous growth of wires. Samples previously coated with 1 nm thick Au film (a) resulted in the growth of thin dense wires compared to the samples with 10 nm thick layer of Au (b). Due to minimization of free energy [19], the diameter of the wires is related to the size of the catalytic droplets formed during the sample annealing. Experiments where Au-coated sapphire substrates were annealed in the furnace without powder using similar temperatures and pressure show that thicker Au catalyst layers form larger catalyst droplets from which the nanowires nucleate. When the droplets reach supersaturation, the ZnO precipitates out as a wire with a diameter that on average follows the diameter of the Au–Zn islands. Dense areas of wires can be reached when thinner catalytic films are used. The formation of a smaller catalytic island implies the formation of a denser island areas.

Differences between the base and tip diameter are clearly more pronounced for samples with thicker catalyst layers. For a 10 nm Au film the initial diameter of the wires/rods decreases by about 50% on average after growing almost 1 μm in height at 3 mbar and 820 °C. This can be explained by changes in the Zn vapour source rate during the experiment. As the source vapour decreases the nanowire diameter seems to drop in size to compensate for the lack of vapour. In addition, larger diameter wires need more vapour to grow and so are more
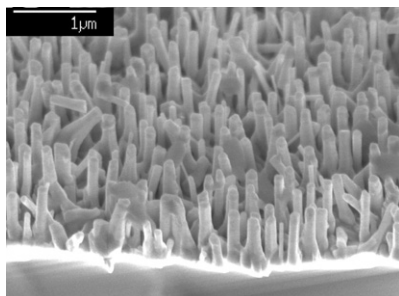
Figure 2. Vertically aligned ZnO nanowires grown on 10 nm Au-coated sapphire substrate at 3 mbar pressure and at temperature of 750 °C, using 27 sccm of purified air.

affected by changes in the amount of Zn vapour being sourced. The average base and top diameter of the wires grown at 3 mbar and 820 °C are 170 and 90 nm for a 1 nm Au film sample and 160–300 and 90 nm for the 10 nm sample.

3.2. Influence of the deposition temperature

Nanowires were grown at several different temperatures while keeping other parameters constant by changing the placement of the substrates upstream or downstream in the furnace. The role of temperature on the structure of the wire is more complex than the direct relation between the catalyst film thickness and the wire diameter. The temperature affects the growth in three ways: the temperature affects the size of the catalyst droplets; it determines how much the vapour would want to condense; and it determines the length of the surface diffusion of the adsorbed vapour species [20].

Beginning with the catalyst droplets, higher deposition temperatures imply the formation of smaller and denser Au–Zn droplets and as a consequence thinner and denser wires. As the temperature decreases, the wires become wider and shorter. Figure 2 shows aligned wires grown using the same conditions as the wires shown in figure 1(b), except for a lower local temperature of 750 °C. At this temperature the wires became wider, shorter and less dense compared to those grown at higher temperatures. The average base and tip diameter are 320 and 250 nm while the height is only 0.7 μm.

The effects of surface diffusion and the condensation of vapour create strong differences in the growth rate in different temperature zones. Figure 3 shows the nanowires grown on a 1 nm Au film at temperatures between 680 and 864 °C. The samples were grown using a constant gas flow of 27 sccm and pressures varying from 1 to 9 mbar.

At very high temperatures, higher than 864 °C (not shown), the nanowires are short with a very low density and small diameter. As the temperature decreases the best conditions occur for 70–100 nm diameter wires which have a high areal density (at 750 and 864 °C for 3 mbar and at 864 °C for 5 mbar). As the temperature continues to decrease the diameter increases to 250 nm and the height decreases from 2 to 0.5 μm. At very low temperatures nanowire growth ceases. Overall, the growth rate actually increases at first and then begins to decrease. At high temperatures ($\sim$900 °C) the growth species is energetic enough to remain in the form of a vapour

and not condense, so there is a high rate of desorption and re-evaporation which leads to short, thin, sparse wires. At the lowest end of the temperature range investigated the substrate temperature seems low enough that the vapour has little energy and the atoms are deposited exactly where they land, creating a rough uneven film [20]. The intermediate temperature zone has enough vapour to grow wires and a temperature where there is enough energy to allow the species energy to diffuse and move to the energetically favourable plane of growth but not so high as to cause much re-evaporation. This zone produces dense and aligned epitaxial wires. Nevertheless, as discussed later, this favourable temperature zone changes with pressure.

3.3. Influence of the deposition pressure

The deposition pressure seems to have the most dramatic effect in changing the morphology of the wires. Varying the pressure from 1 to 9 mbar changes not only the diameter, length and density of the wires but also the morphology of the nanostructures that are grown. In figure 3, a set of samples grown at 1, 3, 5 and 9 mbar is shown. At low pressures (1 mbar), in addition to nanowires, nanobelts and planes, nanowires with forks, and flexible nanobelts, which are all crystalline, are formed.

The pressure strongly affects the supersaturation level of the vapour which is critical to determining the type of growth that occurs. The supersaturation level seems to be higher at low pressures and decreases at higher pressures. This could be because more powder was evaporated at low pressures, as measured by the difference in source weight, creating more vapour. This could also be because the concentration of vapour is higher at lower pressures.

At low pressures, this higher supersaturation leads to secondary nucleation and different types of growth since the environment is far away from thermal equilibrium [21]. According to Ye *et al* [21], this non-equilibrium kinetic growth may create a low-surface-energy tip which allows molecules to diffuse away easily to energetic side surfaces causing the growth of nanobelts and sheets and platelets.

When the pressure is increased to 3 mbar, the amount of vapour and oxygen forms well-aligned wires at temperatures between 680 and 864 °C. In this area the supersaturation may be low, allowing anisotropic growth at an energetic nanowire tip but no nucleation on the sides, so growth only happens in one direction. For higher pressures the ZnO condensation range is translated to higher temperature zones. This occurs because at higher pressures there has to be more vapour to maintain the correct concentration, which is possible at higher temperatures. As a consequence, a lack of nanowire deposition is observed for temperatures below 680 °C at 5 and 9 mbar. At these pressures the favourable condition for well-aligned nanowire growth is translated to even higher temperatures and an increase in diameter is observed. As the diameter of the wires increases, the length decreases because of the larger amount of vapour needed to grow thicker wires.

3.4. Influence of the incoming gas flow

The influence of changing the incoming gas flow is important because it can change the relative oxygen concentration inside the tube, especially when the amount of oxygen in the
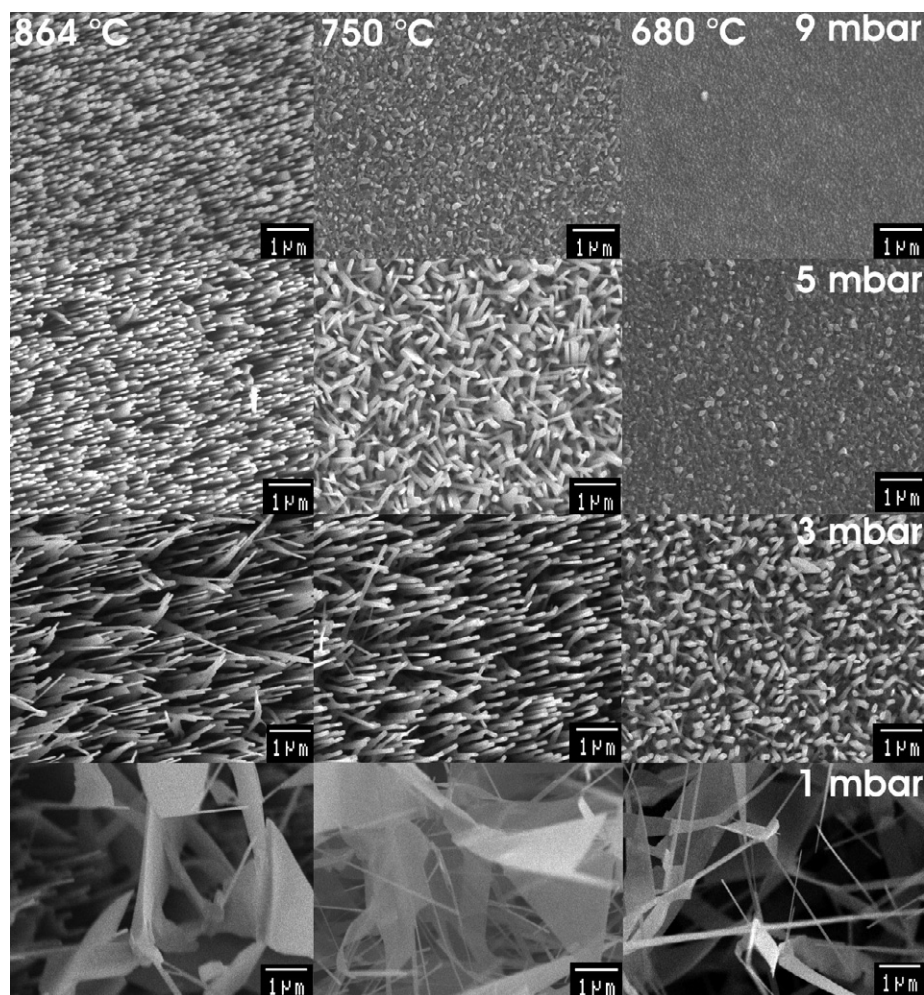
Figure 3. ZnO structures grown at different conditions of pressure and temperature using the same gas flow (27 sccm) and Au catalyst thickness (1 nm).

incoming gas is changed [22]. The variation in the oxygen partial pressure directly affects the process of reoxidation of the Zn vapour and therefore the growth characteristics. In these experiments we used purified air with a constant oxygen concentration of 21%; the pressure inside the tube was kept constant by throttling the pump while investigating the effects of different flow rates and therefore slightly different oxygen/Zn ratios.

Figure 4 shows a composite of SEM micrographs of samples grown at different temperatures at a constant pressure of 5 mbar with the gas flow varying from 17 to 37 sccm. It is possible to observe that at lower flow rates there are smaller rods, which have a lower areal density and are greater in diameter. When the flow rate is increased a slight increase of the relative O/Zn concentration seems to boost growth and create longer wires. The well-aligned nanowires grow where there is a specific match between the ratio of oxygen to Zn vapour. For higher flow rates the extra oxygen may create a greater concentration of growth species by oxidizing the Zn vapour more quickly. This would lead to a higher supersaturation, which leads to extraneous nucleation and different morphologies of growth. At very high flow rates the temperature range for aligned growth decreases as the

concentration of vapour is too high and the area of low supersaturation needed for nanowire growth is moved to lower temperatures; this is similar to the phenomenon of the temperature range for aligned growth changing with pressure.

At very high pressure, where the growth is stable and forms well-aligned nanowires, increasing the oxygen partial pressure seems to create extra nucleation and nanostructures such as triangles and nanobelts.

3.5. Crystalline structure of the nanowires

The crystalline structure of the nanowires was verified using a JEOL 3011 TEM. The nanowires were seen to be crystalline throughout. The hexagonal shape of the wires was evident. Changes in diameter along the length of the wire seem to occur at different points along the nanowire. This could be because of a local decrease in the amount of Zn and oxygen vapour where the supply would only be enough for a smaller diameter wire. No Au catalyst droplet has been seen on the nanowire tips. As the coefficient of thermal expansion for ZnO is much smaller than that of Au, it is possible that the Au droplet may shrink more and fall off of the nanowire, although this may not be likely as none of the nanowire tips show any traces of Au.
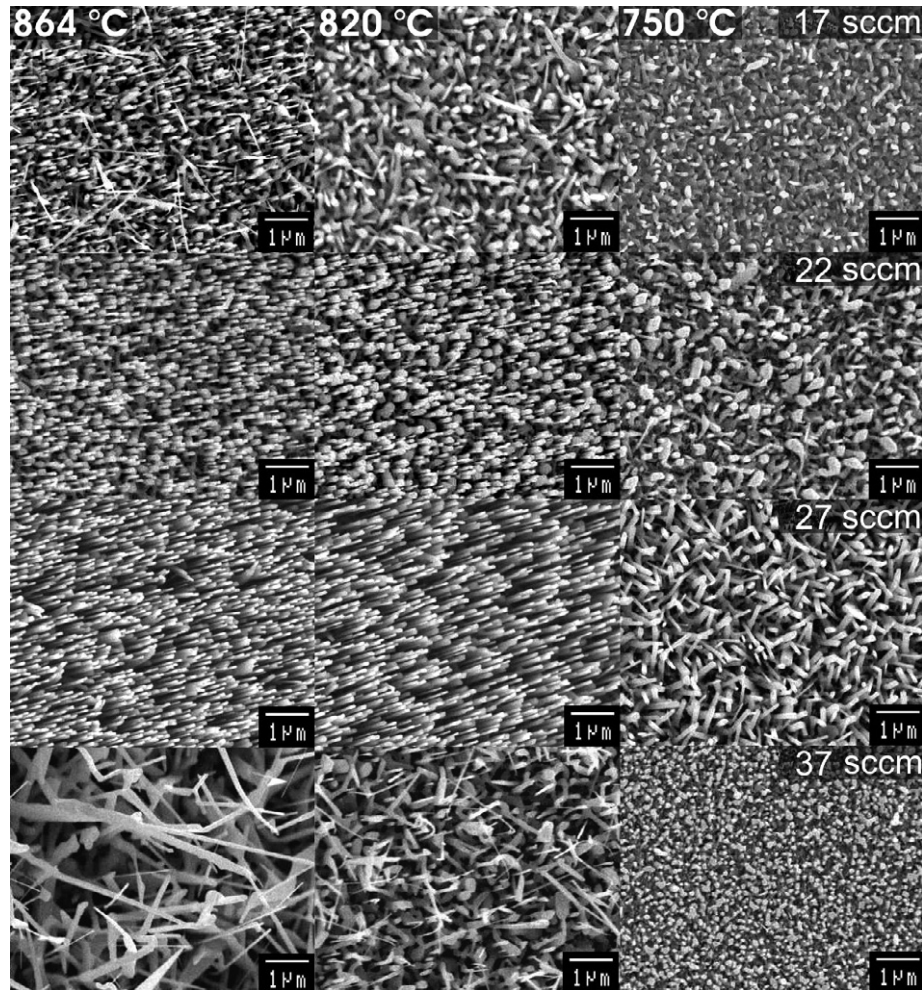
Figure 4. ZnO samples grown at different temperatures and constant pressure of 5 mbar with gas flow varying from 17 to 37 sccm. All samples were previously coated with 1 nm Au film.
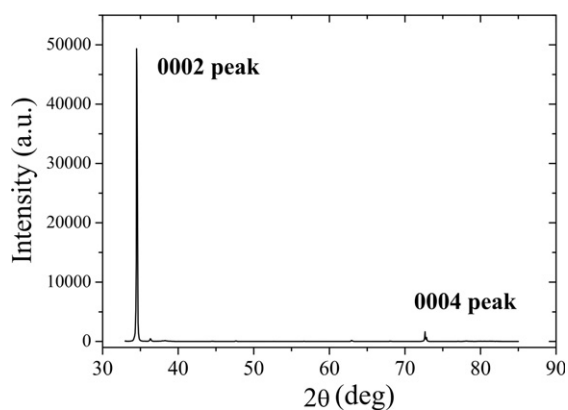

Figure 5. X-ray diffraction pattern of ZnO nanowire on a sapphire substrate. Only multiples of the (0001) peak are seen confirming growth in that direction.

Preliminary secondary ion mass spectroscopy results, which detects in the ppm–ppb range, show no presence of Au at the tip but a large Au peak at the level of the substrate. This creates doubts about the exact mechanism of growth. It seems that the

Au may remain near the substrate and allow a bottom-up (base-growth) type of growth.

Figure 5 shows a typical XRD pattern of the grown nanowires. The XRD confirms that the wires are highly crystalline. Only multiples of the (0001) peaks are seen, implying that all of the wires are well aligned in the growth direction. HRTEM of the samples, such as that shown in figure 6, confirms their crystallinity. In addition, the spacing between lattice fringes is measured to be the 2.65 ± 0.5 Å, which corresponds to the distance between two (0002) planes further confirming the $\langle 0001 \rangle$ growth direction. The ZnO a-axis and the sapphire c-axis are almost exactly related by a factor of four with only a 0.08% mismatch. This allows the ZnO wires to grow in the c-direction epitaxially from the substrate.

3.6. Phase diagram and growth kinetics

Our results showed that the alignment regime of ZnO nanowire growth is very sensitive to the experimental conditions. The control of the Zn reoxidation and condensation kinetics seems to be the key to achieving controllable well-aligned growth. As discussed before, a specific level of low supersaturation of Zn
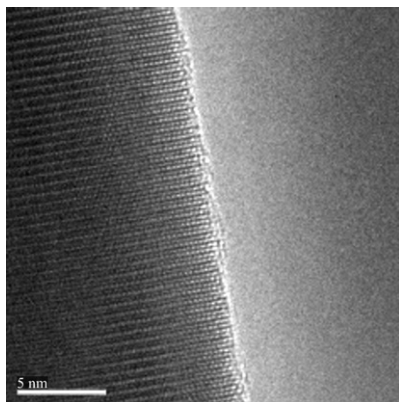
Figure 6. HRTEM of an individual ZnO nanowire whose lattice spacing shows growth in the ⟨0001⟩ direction.
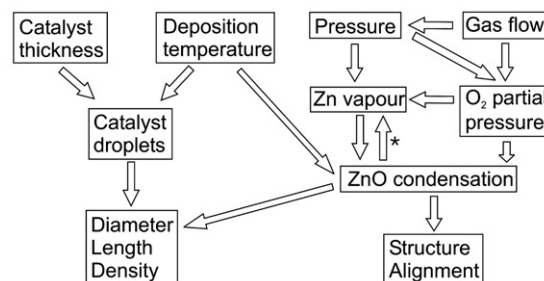

Figure 7. Flow chart describing interdependence relations between variables involved in the growth. The scheme shows the relations observed in our experiments. The effect of other variables such as the ZnO/C powder ratio is not shown.

and oxygen vapour are both necessary to ensure the correct rate of growth, which then leads to having thin and dense aligned wires. Nevertheless, a general model for the entire kinetics of growth at different conditions has not been achieved yet. The interdependences between variables involved in the growth increase the complexity of the process. As a consequence different routes of growth may be found leading to other zones of alignment.

Many papers on the growth of ZnO nanowires seem to use very low oxygen concentrations and high pressures, whereas our oxygen flow is 21% [22]. Song *et al*, for instance, found an alignment zone of growth at 30 mbar using 2% of oxygen in a 50 sccm gas flow [22]. Nevertheless, it is possible to note that the optimum condition found by Song implies the use of relatively high pressure compared to our work. The higher pressure seems to compensate for the low oxygen flow, giving rise to similar oxygen partial pressures to that used in our work. This demonstrates why it is necessary to understand the behaviour of the variables involved in the growth and their interdependences.

In this way, figure 7 shows a flow chart that describes some of the interdependent relations found in our experiments. The growth structure and alignment seem to be directly related to the ZnO condensation kinetics. The kinetics are influenced by the local deposition temperature, total pressure, the amount of Zn vapour and the oxygen partial pressure. The oxygen partial pressure is dependent on the total pressure and on the gas flow when the concentration of the oxygen mixture is changed. On the other hand, the generation of Zn vapour involves complex processes governed by carbothermal reactions which are sensitive to the furnace temperature, the oxygen partial pressure and the ZnO/C powder ratio as well as their grain size and density. The main reaction equations in the carbothermal process can be described as:

$$ZnO_{(solid)} + C_{(solid)} \leftrightarrow Zn_{(vapour)} + CO_{(gas)} \quad (T > 970\,°C) \tag{1}$$

$$2C + O_2 = 2CO \tag{2}$$

$$2CO + O_2 = 2CO_2 \tag{3}$$

$$2Zn + O_2 = 2ZnO. \tag{4}$$

The carbothermal reaction involves oxygen reduction of the ZnO powder by carbon, generating Zn vapour (1). The process is sensitive to the amount of surface contact between ZnO and carbon grains since it defines the active area of the reaction [8]. The oxygen partial pressure can also play an important role since direct oxygen reactions between carbon and oxygen can occur, leading to formation of CO and/or CO_2 by (2) and (3). Depending on the amount of CO a reverse oxidation reaction with Zn at temperatures higher than 900 °C [23] can happen, affecting the amount Zn vapour that is released. Equation (4) represents the Zn reoxidation and condensation processes during the supersaturation of the Zn–Au droplet alloy leading to the growth of ZnO wires. This condensation process is also influenced by the local temperature of growth. More condensation occurs at some temperatures, resulting in a reduction of the available Zn vapour at other temperature zones.

The different types of ZnO nanowire growth are summarized in the phase diagram presented in figure 8, similar to the one by Song *et al* [22]. The nanowire descriptions are a function of temperature and pressure at a constant gas flow of 27 sccm. The diagram was constructed through the use of several experimental points that are indicated in the diagram by black open squares. The respective SEM images of some experimental points are shown in figure 3. The different colours represent five areas of distinct types of growth.

One can imagine the different range of colours as varying degrees of the level of supersaturation of the oxygen and Zn vapour species. The blue areas are at the highest level of supersaturation while the grey areas are at the lowest. Excluding the blue area at 1 mbar, the level of supersaturation seems to follow a curve where it is low and then increases at the region of the well-aligned nanowire growth and then decreases again until the lowest grey level is reached.

Beginning from the bottom of the phase diagram, at low pressure (<2 mbar) there is a blue zone in which ZnO nanostructures of various morphologies such as branched wires, sheets and nanobelts are grown. ZnO has three types of fast growth direction which allow a wide range of structures [24]. At low pressures where the supersaturation level of both oxygen and Zn vapours is higher, growth occurs in more than one direction causing the growth of nanoplatelets, nanosheets and nanobelts.

At higher pressures there are four diagonal bands of growth through the phase diagram. At the highest temperature not much growth occurs. This may be because the reaction
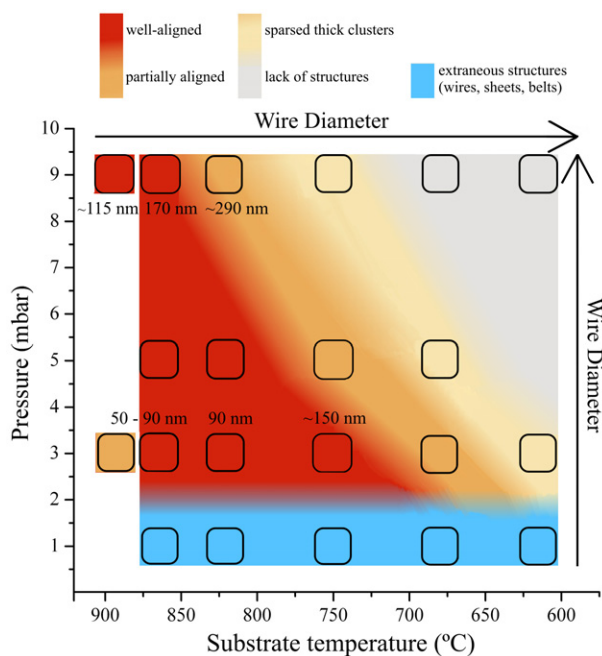
Figure 8. Phase diagram of pressure and temperature showing five main zones of growth. The experimental points are represented by open black squares. The respective SEM images of some experimental points are shown in figure 3. The diameters of the aligned wires grown at 3 and 9 mbar are indicated.

between the ZnO and carbon which frees the Zn vapour is reversible above 900 °C or because of large amounts of re-evaporation [23]. The bands are diagonal due to the need to maintain a certain supersaturation/concentration of vapour species as discussed in section 3.3.

Well-aligned nanowire growth occurs in the red band which begins as a broad band ranging from 680–850 °C. This band narrows as the pressure increases. At higher pressures the area of optimal supersaturation may become smaller since the vapour species diffuse together at the optimal levels for a shorter distance. Thus at lower temperatures at the same pressure the lower level of vapour species creates shorter and sparser wires until there is no structure at all.

The orange zone contains partially aligned wires which occur at lower temperatures adjacent to the red zone. At lower temperatures the diffusion length of the adsorbed species decreases, which decreases the probability of them reaching the exact position in the crystal tip that causes the growth to tilt in different directions. At higher temperatures at 3 mbar a similar type of growth occurs. The higher temperature allows for re-evaporation into vapour, so the number of species available would be lower causing less perfect growth.

The decrease in diffusion length and the change in the correct ratio of Zn:O vapour species may also explain why in the light yellow areas the growth leads to thicker wires instead of longer wires since the adsorbed species may attach to the side of the crystal surfaces instead of all diffusing to the tip to make the wire longer.

The grey area becomes larger with higher pressure. In addition at higher pressures there may be no supersaturation of both the Zn and oxygen species. In this area bulk crystal growth may occur instead of anisotropic nanostructure growth.

A similar phase diagram could be constructed using the oxygen partial pressure and the temperature as variables. The level of supersaturation must not only be correct for one growth species, but for both growth species. The red areas in such a diagram would be at 27 sccm where they would match.

The diameter, length and density of the wires are primarily defined by the size and density of the catalyst droplets. The thickness of the catalyst film as well as the deposition temperature will determine the configuration and size of the catalyst droplets and then the initial stages of growth (sections 3.1 and 3.2). Nevertheless, the kinetics of the ZnO condensation and therefore the pressure and oxygen partial pressure also play an important role in the control of the wire diameter, length and density (as discussed in section 3.3).

4. Conclusions

The process conditions for the growth of vertically aligned ZnO nanowires were studied as a function of the catalyst layer thickness, the deposition temperature and pressure and the oxygen partial pressure. The annealing of the catalyst layer causes the layer to ball into small islands from which nanowires of similar diameter will grow. The island size contributes not only to the diameter, but also to the areal density and the length of the wire. The favourable temperature zone for alignment can be changed by varying the pressure and the oxygen partial pressure. By controlling such parameters aligned nanowires/rods with different diameter and length can be grown reproducibly. The zone with the most well-aligned wires is at a pressure of 5 mbar at approximately 800–860 °C with a 27 sccm gas flow. The growth appears to be occurring through a vapour–liquid–solid process but this still needs to be confirmed.

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