Controlled Growth of Aligned ZnO Nanowires

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ABSTRACT

The growth of vertically aligned zinc oxide nanowires (ZnO NW) using a simple vapor deposition method system is reported. The growth properties are studied as a function of the Au catalyst layer thickness, pressure, deposition temperature, and oxygen ratio. It was found that the diameter and density of the nanowires is controlled mostly by the growth temperature and pressure. The alignment of the nanowires depends on a combination of three factors including the pressure, temperature and the oxygen ratio. Our results implicates the growth occurs by a vapor liquid solid (VLS) process [1].

Keywords: zinc oxide, nanowire, vls

1 INTRODUCTION

Zinc oxide a direct wide bandgap semiconductor (~3.3eV) is the focus of much research due to its potential in fabricating light emitting diodes [2], sensors [3], and uv laser diodes [4] due its large exciton binding energy (~60meV) which is more than two times higher than thermal energy at room temperature. It also has uses as a piezoelectric [5] and transparent conducting material [6], as well as a potential diluted magnetic semiconductor (DMS) [7].

A wide variety of zinc oxide nanostructures have been grown such as nanowires [1,8], nanobelts [9], tetrapods [10], nanorings [11] and nano-combs [12]. Zinc oxide 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 vapor deposition [15], and metal organic vapor phase epitaxy [16]. Being able to control the diameter and length of the nanowires is integral to many applications. By vaporizing a mixture of zinc oxide 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.

The growth parameters responsible for the aligned growth are not clear. The kinetics of the reactions during carbothermal reduction and the re-oxidation leading to formation of ZnO wires is complex and involves many inter-dependent variables. The temperature as suggested by many papers does not only define the conditions for alignment but involves a complex inter-dependence of variables, which define specific vapor conditions. Therefore a general understanding of the conditions that control the growth is crucial in achieving reproducibility in vertically aligned growth, which is essential for many applications involving ZnO nanowires.

In this paper, we report the growth of vertically aligned nanowires using a physical vapor deposition process with Au as the catalyst. In order to identify the best aligned growth conditions we have performed a study of the effects of the various parameters that affect the growth of the aligned ZnO nanowires. Specifically, we investigated the effects of catalyst layer thickness, the deposition temperature and the oxygen partial pressure present on the diameter, density and structure of the nanowires. After growth the wires were characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HREM), and XRD. A discussion about the best condition for aligned growth and its relation with the reaction kinetics is presented.

2 EXPERIMENT

The ZnO nanowires were grown by heating zinc oxide and graphite powders in a furnace at 1000°C. The sapphire substrates were cleaned and then annealed at 1000 °C to remove any defects. The substrates were then coated with a thin film (1-10nm) of gold using a thermal evaporator.

After the catalyst layer has 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. A 1:1 mixture by weight of ZnO:C was weighed and placed into a separate quartz boat upstream from the substrates at the hottest point of the furnace. The tube was then pumped down to a base pressure of 10⁻² mbar using a rotary pump. A purified air mixture gas consisting of 21% oxygen was then flowed into the chamber increasing the chamber pressure to 3x10⁻¹ mbar, corresponding to gas flow of 190 sccm. The deposition pressure is then set to between 1 and 9 mbar. The furnace was heated at 60 degrees per minute; after reaching 1000 °C the substrate was left to anneal for 30 minutes. After the deposition, during cooling the airflow direction and pumping direction were reversed to prevent any growth at other temperatures.
The SEM studies were performed on JEOL 6340F FEGSEM operated at 5kV. The 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 isopropanol ultrasonic bath and placing them onto holey carbon grids.

3 RESULTS AND DISCUSSION

Figure 1 shows a typical XRD of the nanowires grown. 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 2 confirms their crystallinity. In addition, the spacing between lattice fringes is measured to be the 2.65± 0.5 Å that corresponds to the distance between two (0002) planes further confirming the <0001> growth direction.

The alignment regime in the ZnO nanowires growth on sapphire is very sensitive to the experimental conditions. A set of variables such as the local temperature, pressure and oxygen flow seems to have great influence on the growth. Several structures can be created and different alignment zones can be found by varying such variables.

Our work suggests that the initial Au catalyst thickness does not affect drastically the alignment of the wires. However, the thickness of the layer seems to directly affect the diameter of the nanowires as well as the areal density. Samples previously coated with 1 nm thick Au film resulted in the growth of dense thinner wires compared to the samples with 10 nm thick layer of Au. As discussed previously [18], the diameter of the wires is related to the size of the catalytic droplets formed during the sample annealing. The thicker Au catalyst layer forms larger catalytic droplets from which the nanowires nucleate. When the droplets reach supersaturation, the ZnO precipitates out as a wire with diameter following, on average, the diameter of the Au-Zn islands. Dense areas of wires can be reached when thinner catalytic films are used. The formation of smaller catalytic island implies the formation of denser island area.

Differences between the base and tip diameter are clearly more pronounced for thicker catalyst layers samples. 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. These phenomena can be explained by changes in the Zn vapor source rate during the experimental time. As the source vapor decreases the nanowire diameter seems to drop in size to compensate for the lack of vapor. In addition, larger diameter wires need a larger quantity of vapor to grow and so are more affected by changes in the amount of Zn vapor 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 a 10 nm one.

The role of temperature on the wire structure is more complex than the direct relation between the catalyst film thickness and the wire diameter [19]. On the one hand, higher deposition temperatures imply the formation of smaller Au-Zn droplets and as consequence thinner and denser wires. As the temperature decreases, the wires become wider and shorter.
On the other hand, the local temperature determines the condensation power of the Zn vapor, consequently, a strong difference in the ZnO growth rate at different temperature zones in the quartz tube. Figure 3 shows the nanowires grown on 1nm Au films at temperatures between 680 and 864 °C. The samples were grown using a constant gas flow of 190 sccm and pressures varying from 3 to 9 mbar. It is possible to observe differences in the growth rate for each temperature, especially at higher pressures. 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 where there are 70-100 nm diameter wires and high areal density (at 750°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...
2µm to 0.5 µm. At very low temperatures the growth of nanowires ceases. Overall, the growth rate actually increases at first and then begins to decrease. At high temperatures the vapor may not want to condense very much which leads to short thin sparse wires. At low temperature the vapor condenses without forming structures. There is an intermediate temperature zone with specific condensation ratio where it is possible to get dense and well aligned wires. Nevertheless, as discussed later, this favourable temperature zone changes as the pressure is changed.

The deposition pressure seems to have the most dramatic effect in changing the morphology of the wires. Varying the pressure from 1 mbar to 9 mbar can form a wide range of structures as well as wires with different diameter, length and density. In Fig. 3 a set of samples grown at 1, 3, 5 and 9 mbar is presented. At low pressures (1 mbar) the morphologies of the nanowires changes into different types of morphologies such as nanobelts and planes as well as nanowires with forks and very thin wavy structures which are still crystalline. At low pressures more of the powder is actually evaporated according to the amount that is evaporated by weight. This increase in the amount of vapor causes the extra growth allowing faster, less structured growth instead of the slower growth needed for nanowires. In addition, the mean free path of the vapor in the tube is larger at low pressures resulting in ZnO condensation even at lower temperatures.

When the pressure is increased to 3 mbar, the amount of vapor and oxygen forms well-aligned wires at temperatures between 680 and 864 °C. For higher pressures the ZnO condensation range is translated to higher temperature zones. As consequence, a lack of nanowire deposition is observed for temperatures below 680 °C at 5 and 9 mbar. At those pressures the favorable condition for well-aligned wires growth is translated to even higher temperatures and width increases on the diameter is also observed. As the diameters of the wires increase, the length also decreases because of a lack of enough vapor to grow higher.

These phenomena could be attributed to the change in the oxygen partial pressure. The oxygen partial pressure is important because it determines the amount of zinc vapor that is released that becomes re-oxidized to form the zinc oxide nanowires. The higher the pressure in the tube the greater the oxygen concentration since the amount of incoming gas is constant. Well-aligned nanowires are reached at specific conditions of pressure and temperature when the Zn/O ratio and the condensation velocity are in the correct proportions. Higher oxygen partial pressures imply a higher level of Zn re-oxidation. At very high pressure, where the growth is stable and well-aligned nanowires are formed, increasing the oxygen partial pressure seems to create extraneous nucleation and nanostructures such as triangles and nanobelts.

4 CONCLUSIONS

The process conditions for the growth of vertically aligned zinc oxide 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 conditions for alignment involve a complex inter-dependence of variables, which define specific vapor conditions. The favourable temperature zone to alignmet can be changing 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 growth still seems to be occurring through a VLS process but this still needs to be determined.

REFERENCES