Vapour transport growth of ZnO nanowires using a predeposited nanocrystalline template

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Abstract. Vapour transport growth of ZnO nanowires has been reported by a few groups. In most of the vapour transport deposition processes, 1-D ZnO nanostructures were produced at relatively high temperature (>900°C) and a pre-deposited catalyst, such as Au, Co, or Sn, was needed to supply nucleation sites and provide the function of growth direction confinement. Here we have produced single crystal ZnO nanowires using a modified vapour transport method, in which a nanocrystalline ZnO template layer was first deposited by ultrasonic spray assisted chemical vapour deposition. The pre-deposited template was then used to grow ZnO nanowires by a traditional vapour deposition method. The nanowires were characterised using X-ray diffraction, field-emission gun scanning electron microscopy (FEG-SEM) and high-resolution transmission electron microscopy (HRTEM). Several different morphologies of the ZnO nanowires, including branched wire growth, were observed and a possible growth mechanism was discussed.

1. Introduction

ZnO, with a direct band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV [1], is of considerable technological importance because of its potential use in short-wavelength devices, such as ultraviolet (UV) light-emitting diodes and laser diodes. The fabrication and application of 1-D ZnO nanostructures have therefore attracted considerable interest in recent years. Notably, ZnO nanowires have been demonstrated in room-temperature UV lasing [2]. Recently, a high-temperature solid-vapour process has also been reported to produce polar-surface dominated ZnO nanobelts and electrostatic energy induced nanohelixes, nanosprings, and spiral nanostructures [3]. In most of the vapour transport deposition processes, the 1-D ZnO nanostructures were produced at relatively high temperature (>900°C) and a metal catalyst is normally needed, such as Au [2], Co [4], and Sn [5]. Several low-temperature growth processes have also been reported earlier, such as a wet chemical route [6], sol-gel electrophoretic deposition [7], and electrochemical growth [8]. Very recently, we have developed an ultrasonic spray assisted chemical vapour deposition method for ZnO nanowire growth, which is self-catalysed by Zn droplets on the surface of a nanocrystalline ZnO seed layer [9].

In this paper, we produce ZnO nanowires using a modified vapor transport method, in which a uniform nanocrystalline ZnO seed layer was first deposited by ultrasonic spray assisted chemical

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vapour deposition and ZnO nanowires were then grown on top of the seed layer by vapour transportation.

2. Experimental
The seed layer was produced by the method described in our recent publication [9]. Solutions of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) in a mixture of methanol/ethanol and deionised water with different concentration were prepared in advance as a stock precursor solution. The precursor aerosol was generated from the vibrations of the transducers and was delivered towards the heated substrate by the carrier gas Ar. The gas flow rate used was between 0.5 and 5 l/min. The aerosol vapour was delivered to a hotplate where a substrate was fixed. The temperature was controlled using K-type thermocouples. After the deposition of the seed layer, the seeded substrate was placed into a downstream position and lower temperature zone (<600°C) in a quartz tube furnace, in which a alumina ceramic boat was placed filled with a ZnO and carbon powder mixture (ZnO:C=2:1). The furnace temperature was then increased to 900°C and Ar gas was introduced into the tube furnace with a flow rate of 1 l/min for 1-2 hours. In this way, the ZnO nanowires were found deposited on the seeded substrate.

The deposited products were characterised by X-ray diffraction (XRD) (Phillips X’pert diffractometer), with Cu Kα radiation (λ= 0.154178 nm at 40 kV and 40 mA), and field emission gun scanning electron microscopy (SEM) (JEOL 6340F) with an accelerating voltage of 5 kV. High resolution transmission electron microscopy (HRTEM) (JEOL 4000EX-II), operating at 400kV, was also used to characterise the resultant nanowires.

3. Results and discussions
Figure 1(a) shows a typical SEM image of the ZnO seed layer deposited at 400 ºC with a precursor concentration of 0.005 M. The seed layer apparently consists of nanocrystalline ZnO grains. The grains are of about 50-80 nm in size with an elongated shape. Figure 1(b) shows the XRD pattern of the seed layer. The results show that the seed layer is pure single ZnO phase. The diffraction pattern can be indexed as the hexagonal wurtzite structure of ZnO. The calculated lattice constants are \(a = 3.25 \text{Å}\) and \(c = 5.21 \text{Å}\), which are in good agreement with the JCPDS file of ZnO. No preferred orientation was found in the seed layer; and this is expected with the use of amorphous glasses as substrates and the relatively high growth rate.

![Figure 1](image_url)

Figure 1. (a) FEG-SEM image of ZnO seed layer; (b) XRD pattern of ZnO seed layer.

After a further vapour transport deposition inside a tube furnace, ZnO nanowires were formed. As shown in Figure 2(a), ZnO nanowires start to form just after 20-minute further deposition on top of the seed layer. Deposition for longer time produced not only more nanowires, but also longer nanowires.
as shown in figure 2(b). The average diameter of the ZnO nanowires is around 80 nm, namely about the same size of the seed grains, which implies that the size of the nanowires depends on that of the seed grains. Different morphologies of ZnO nanowires can also be observed in the samples with long deposition times, such as branched nanowire in figure 2(c) and stacked platelets on a nanowire tip in figure 2(d).

Unlike most of the vapour-liquid-solid (VLS) processes, in which hetero-catalysts are involved, in this process the predeposited ZnO seed or template has the same composition as the final ZnO

Figure 2. FEG-SEM images of ZnO nanowires. (a) deposited for 20 minutes; (b) deposited for 60 minutes; (c) a branched ZnO nanowire in the longer time deposited sample; (d) stacked ZnO platelets formed on a tip of a ZnO nanowire; (e) EDX spectra of both ZnO seed layer and nanowire.
nanowires, thereby avoids contamination from foreign elements in a catalyst. Energy dispersive X-ray spectrum (EDX) analysis results in Figure 2(e) indicate the same composition in both seed layer and nanowires, which also confirm that the nanowires are indeed ZnO. It should be noted that Si signal in the seed layer spectrum comes from Si substrate.

The single crystalline nature of the final ZnO nanowires was revealed by transmission electron microscopy. Figure 3(a) shows a HRTEM image of a ZnO nanowire of 76 nm in diameter, which shows the perfect hexagonal crystal structure. Both the HRTEM image in Figure 3(a) and the diffractogram in figure 3(b) show that the nanowire grows along the ZnO $c$-axis. The lattice spacing measured from HRTEM image corresponds to that of ZnO.

![HRTEM image and diffractogram of ZnO nanowire](image)

Figure 3. (a) HRTEM image of a ZnO nanowire of 76 nm in size; (b) diffractogram of the nanowire showing the growth direction along [0001].

The results here indicate that this modified vapour transport method is a good alternative to traditional VLS growth, in which an external catalyst, such as Au, is often required. The key of the process presented here is apparently the predeposited nanocrystalline seed layer. By using lattice-matched substrate, e.g. sapphire, we should be able to grow vertically aligned ZnO in this way.

4. Conclusions

Single crystalline ZnO nanowires have been successfully produced using a modified vapor transport method, in which a uniform nanocrystalline ZnO seed layer was first deposited by ultrasonic spray assisted chemical vapour deposition and ZnO nanowires were then grown on top of the seed layer by vapour transportation. This method proves to be a relative simple and clean process, since no external catalyst is used.

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