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Aqueous synthesis of interconnected ZnO nanowires using spray pyrolysis deposited seed layers

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ABSTRACT

Interconnected ZnO nanowires were grown in a two-stage process, using spray pyrolysis deposited ZnO seed layers as a nucleation platform for subsequent hydrothermal growth. We present a comparison between the effect of these spray pyrolysis deposited seed layers and well-ordered sputter deposited seed layers, along with their respective ZnO nano-morphologies that were obtained via hydrothermal growth. It will be shown that the growth of interconnected ZnO nanowires was influenced by the physical and crystallographic orientations of the underlying seed crystallites. Sputtered seed layers resulted in fairly vertical nanorods which were approximately 80 nm in width, while seed layers deposited by spray pyrolysis resulted in arrays of interconnected ZnO nanowires measuring approximately 15 nm in width.

1. Introduction

Many different morphologies of low dimensional ZnO structures have been synthesized in gaseous and liquid environments [1]. It has been demonstrated that nanostructured ZnO is a suitable candidate for many applications including: piezoelectric power generation [2], resonators and cantilevers [3,4], one-dimensional transistors [5], gas sensing [6], biosensing [5,7], electrowettable surfaces [8], optical devices [9,10], solar cells [11], and many others [12]. However, controlled fabrication of one-dimensional metal oxide nanostructures is still one of the most important technological hurdles for the development of ZnO based nanodimensional devices.

The deposition of interconnected ZnO nanostructured arrays onto glass substrates is a two-stage process: i) the deposition of a ZnO seed layer via spray pyrolysis for the formation of an angular seed layer [13], and ii) a subsequent hydrothermal growth step by our modified method based on the pioneering work of Vayssieres [14]. This two-stage synthesis is relatively “environmentally” friendly, scalable, inexpensive, and can be applied to a variety of different substrates. A comparison of ZnO nanostructures grown from RF sputtered seed layers and layers deposited by spray pyrolysis will also be presented.

ZnO deposition via spray pyrolysis [15,16] was adopted for the synthesis of rough seed layers, and as will be shown, was found to be critical in the formation of an interconnected one-dimensional ZnO morphology. Additionally, as a process, it has many advantages such as: effective stoichiometry control, excellent homogeneity, relatively low processing temperature, and low cost fabrication for large area films [15,17].

2. Experimental/method

In this two-stage process, ZnO seed layers were first deposited onto rotating glass substrates at 450 °C using a typical spray pyrolysis deposition system [13]. The precursor solution (100 mL) was prepared by dissolving 0.15 M of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] in a solvent mixture of double DI water and isopropyl alcohol with a 1:3 volume ratio. To enhance the solubility of zinc acetate, 0.4 mL of acetic acid was also added to the solution. This solution was sprayed onto substrates through a 0.2 mm nozzle, using a N_2 carrier gas. ZnO thin films were deposited on rotating (25 rpm) hot substrates; the solution flow rate, carrier gas pressure and nozzle to substrate distance were held constant at 10 ml/min, 2 atm and 40 cm, respectively. The deposited seed layer thickness was determined to be approximately 300 nm using an Ambios-Technology XP-2 profilometer. To compare the influence that different seed layers have on the resultant nanostructures, multiple glass substrates were also covered with a ~1.2 µm ZnO seed layer deposited by RF sputtering. The sputtering conditions included: target to substrate distance of 7.5 cm, and sputtering power of 100 W in a process gas of 60% N_2/40% O_2, at 260 °C.

During the second stage of deposition, ZnO nano-morphologies were grown in a sealed reaction vessel via the hydrothermal

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decomposition of hexamethylenetetramine (HMT) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) solutions based on a modified method first described by Vayssieres [14]. In this process, glass substrates with sputtered or sprayed seed layers were placed into a sample holder, which were then placed inside a reaction vessel filled with an equimolar solution of a 10 mM HMT/$Zn(NO_3)_2 \cdot 6H_2O$. These vessels were sealed and then placed inside a laboratory oven for 16 h at 80 °C. Following this, the coated glass substrates were removed and washed with DI water to eliminate any residual zinc salts and dried in a stream of N_2 prior to analysis.

The final growth step resulted in high density low dimensional ZnO nanostructures: vertical nanorods where sputtered seeded layers were employed (Fig. 1). Interconnected nanowires emanating from the tips of emerging nanorods were observed in all spray pyrolysis deposited seed layer samples (Figs. 2 and 3). As shown in Figs. 2 and 3 at the terminations of the ZnO nanowires, many nanowires bundle together along the ends of their non-polar crystal facets, with individual nanowires having an average width of approximately 15 nm.

3. Results and discussion

It has been previously shown that ZnO nanostructures grown via hydrothermal means and using highly orientated seed layers tend to adopt the direction of the seed crystallites [18,19]. ZnO seed layers formed via physical vapour deposition processes typically produce highly orientated seed layers [18]. There are also a few other factors that may affect these morphologies and may promote the formation of interconnections between nanostructures. The orientation of the underlying substrates, and hence, the emerging nanorod/nanowire orientation greatly influences the likelihood of forming interconnections between neighbouring structures.

As shown in Fig. 1, the growth of ZnO nanorods from a highly orientated seed layer consisting of regular sputtered crystallites (with hemispherical terminations) resulted in an array of high density ZnO nanorods, which rarely deviate from their perpendicular growth habits. By utilising a rough seed layer deposited by spray pyrolysis, we have facilitated the growth of interconnected nanostructures. The scanning electron micrograph presented in Fig. 2, indicates that the nanowires stem directly from the tip of a ZnO nanorod. The nanowires typically connect with neighbouring structures, resulting in free-standing wire clusters.

Unlike the ZnO sputtered seed layers with periodic hemispherical crystallites, ZnO seed layers deposited via spray pyrolysis are comparatively rougher, typically consisting of sharp polygonal crystallites. As the ZnO nanorods emerge from their underlying seed crystallite they do so perpendicularly, and as the underlying layer is non-uniform, many of the nanorods grow very close to one another; as is schematically represented in Fig. 3. It is possible that the close proximity between the emerging nanorods generates a localised electric field, attracting charged precursors in solution. Thus, promoting rapid growth at the sharp hexagonal tips, resulting in the fine ZnO nanowires that were observed in Fig. 3. This may sustain the rapid growth of ZnO, effectively decreasing the width of the nanostructures, resulting in nanowires: ~15 nm for spray pyrolysis vs ~80 nm for sputtered seed layers. It is also possible that during growth, these tips generate strong dipoles which have the potential to bend the highly flexible piezoelectric nanowire tips towards each other, which later coalesce along the terminations of their non-polar crystal facets.

3.1. XRD investigations of interconnected ZnO nanowires

X-ray diffraction studies of the different seed layers and the effect of hydrothermal treatment are presented in Fig. 4. Here it is clear that the sputtered seed layer has a preferential (002) reflection centered upon 34.4° which is intensified and splits into two well-defined peaks at 34.4 and 34.8° 2θ after hydrothermal treatment. Sprayed seed layers demonstrated comparatively weaker reflections corresponding with (002) and {100} crystal planes. It was observed in sputtered

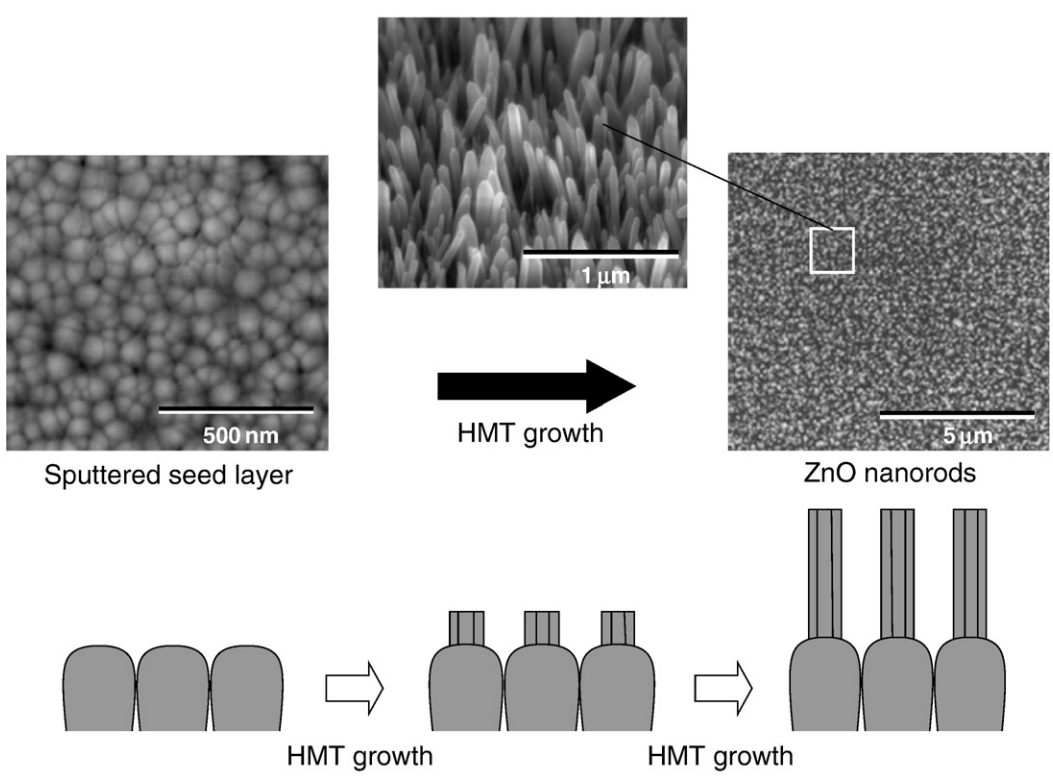

Fig. 1. Different growth stages of ZnO nanorods: (1) RF sputtered seed layer, (2) Initial rod formation from the seed layer, and (3) ZnO nanorods.

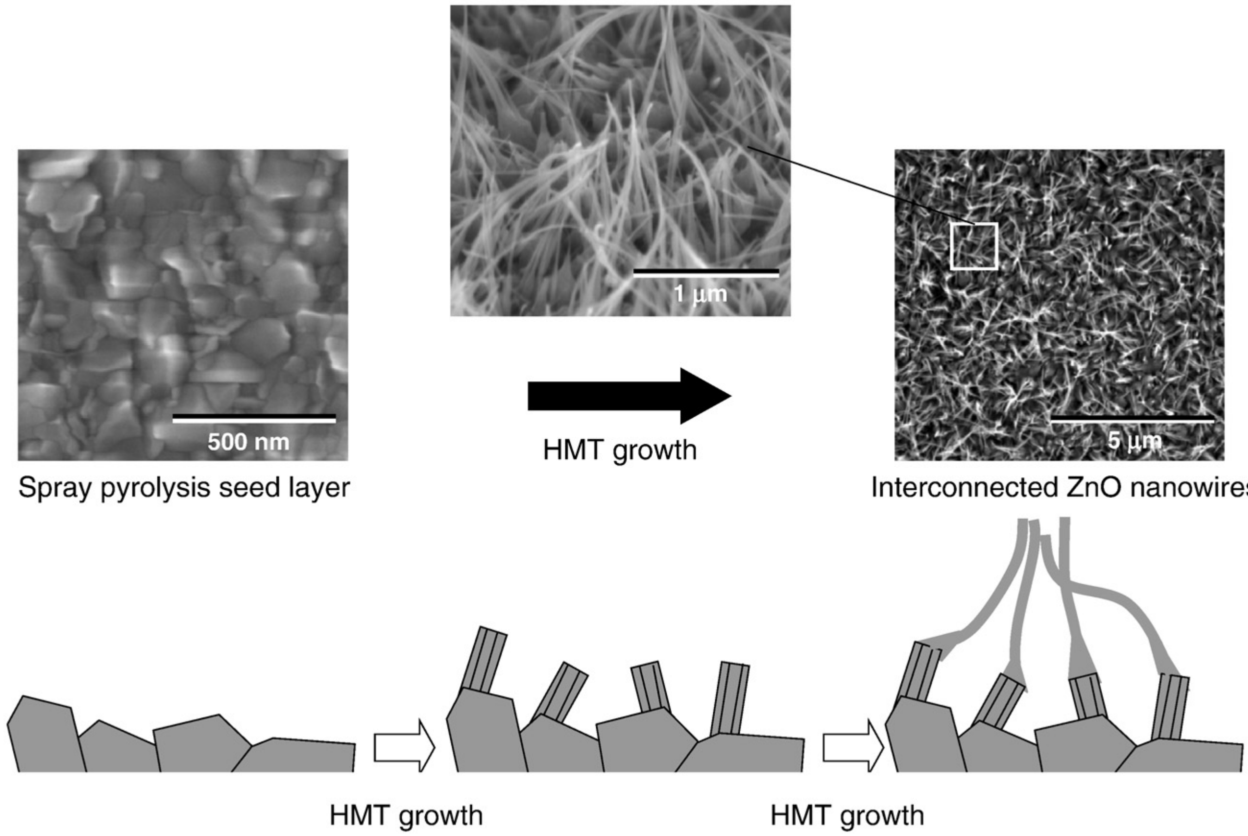

Fig. 2. Different growth stages of interconnected ZnO nanowires: (1) spray pyrolysis deposited seed layer, (2) initial rod formation from the seed layer, and (3) nanowire growth from the extended tips of the ZnO nanorods, which bundle together along their non-polar crystal facets.

films, that the (002) plane was also intensified after hydrothermal treatment, notably, the minor reflections of {100} were also augmented. Thus, confirming that the hydrothermal treatment which results in either free standing or interconnected nanorods adopts the crystallographic orientation of the underlying seed layer. All specimens were in good agreement with ICDD #36-1451 corresponding to wurtzite ZnO, with some minor contributions from ICDD #38-0385 $Zn(OH)_2$ denoted in Fig. 4 as "*".

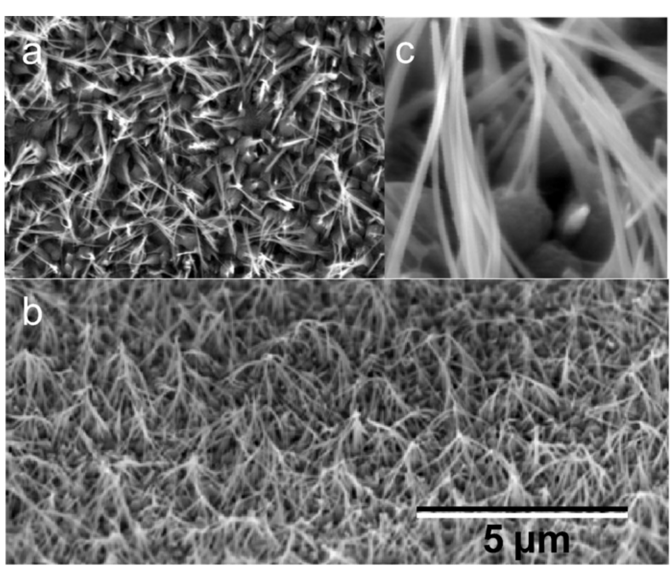

Fig. 3. Interconnected ZnO nanowires: (a) from above, (b) at 45° rotation, and (c) high magnification image of the nanowires bundled along their non-polar facets.

4. Conclusion and further suggestions

Interconnected ZnO nanowires were fabricated on glass substrates. XRD studies revealed that the hydrothermal growth step followed the preferential crystallographic orientation of the underlying seed layer. Electron microscopy observations indicate that the fast growing ZnO nanowires emanate from the tips of larger ZnO nanorods, and these nanowires frequently connect with neighbouring nanowires to form freestanding localised connection hubs. At present, the interconnected ZnO nanostructures do not form contiguous networks, however, it may be possible to engineer interconnects with well-defined orientations by selectively patterning the seed layer surface. By photo-lithographically patterning the underlying substrate, and etching patterns appropriately after spray pyrolysis, it may be possible to implement the observed interconnectivity for the next generation nanodimensional electronic devices. The developed

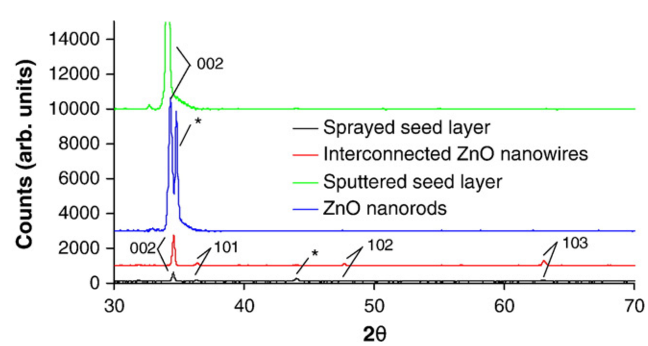

Fig. 4. XRD comparison of ZnO seed layers and the ensuing nanostructures after hydrothermal growth.

process is relatively simple and utilises inexpensive reagents; given the flexibility that spray pyrolysis and hydrothermal growth offer, the presented method is also suitable for large substrates. This method could be used with minor modifications to form other interconnected metal oxide nanostructures by substituting reagents, while accounting for the acidic or basic nature of the target metal oxide.

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