

Growth of ZnO nanotube arrays by hydrothermal methods on ZnO film coated Si substrate

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ABSTRACT: ZnO nanorods (NRs) and nanotubes (NTs) were synthesized by a hydrothermal method on Si substrates that have been pre-coated with a thin ZnO film (by pulsed laser deposition (PLD)). Scanning electron microscopy investigation indicated early formation of Nanorods on the PLD ZnO coating, which is longer and displays higher length /diameter aspect ratios. The morphologies of these nanorods changed significantly over the course of a reaction run, 3-9 hours. Progressively tapering, and producing volcano like surface structures that develop into Nanotubes. High-resolution transmission electron microscopy and selected area electron diffraction analysis confirm that the Nanotubes are ZnO single crystals and that their growth direction is along the C-axis [0001]. To explain the growth of this ZnO, Nanotubes, we have carried out investigations on the effects of the PLD ZnO films and solution effect, on the growth properties of ZnO Nanorods and Nanotubes.

KEYWORDS: Zinc oxide film, Nanorods, Nanotubes, Hydrothermal Growth.

I. INTRODUCTION

ZnO is an excellent opto electronic material [1-5] due to its wide direct band gap (3.37eV) and large excitation binding energy (~ 60 meV). It has been confirmed as a promising functional material in other Nanodevices such as, gas sensors [6] and field emitters [7]. Due to these advantages the synthesis of ZnO Nanostructures is thus currently attracting worldwide attention and numerous ZnO Nanostructures have been demonstrated, for example, nanowires [8] nanotubes [9], nanobelts [10], nanopropellers [11] and nanocages [12]. Amongst these nanostructures, tabular structures are of particular interest due to their unique, defined geometry and to the remarkable range of their potential applications. Several methods of synthesizing tabular ZnO have been demonstrated including hydrothermal methods [13-15] template based growth [16-17] thermal evaporation [18], plasma molecular beam epitaxy [19] and metalorganic chemical vapour deposition [20]. A simple low temperature of 90°C, preparation of zinc oxide 1-dimensional nanomaterials involves the reaction between hexamethylenetetramine (HMT, also termed methenamine) and aqueous zinc ions [9], [13], [21-25]. When substrates precoated with a laser ablated thin-layer of zinc oxide, are placed in this reaction solution arrays of aligned 1-dimensional, crystalline zinc oxide nanostructures are formed. Empirical changes to the reaction conditions have resulted in the growth of nanorods, nanotubes and nanowires on such substrates. Investigations in which zinc oxide has been grown over extended periods of time, several hours have shown that the structures continually evolved from nanorods to nanotubes terminated with nanowires have been observed. Here we report the hydrothermal synthesis of arrays of ZnO nanotubes on Si wafers that had been pre-coated by a thin ZnO film produced by pulse laser deposition (PLD). Highly aligned arrays of such nanotubes can be obtained by critical point drying (CPD) [26] of the as-grown samples.

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II. EXPERIMENTAL SECTION

A. Substrate Preparation.

Borosilicate glass, pt-coated glass, and pieces of Si wafer with and without a thin ZnO coating were all investigated as substrates on which to grow ZnO NRs and NTs. Pt films with thickness $\sim 10\text{nm}$ were coated on glass by thermal (hot filament) evaporation, under vacuum. The ZnO thin films were formed by PLD, using a system that has been described elsewhere [27]. In short, the output of an ArF excimer laser (Lambda-physik compex 201, 193nm, 10Hz repetition rate) was focused on a rotating ceramic ZnO target (cerac, 99.999%), yielding an incident fluence on the target of $\sim 3\text{J}/\text{cm}^2$. Typically, the distance between the target and the Si substrate was $\sim 50\text{mm}$, the background pressure of O_2 within the deposition chamber was $\sim 10\text{m Torr}$, and the substrate temperature (T_{sub}) was maintained at $\sim 300^\circ\text{C}$ by illuminating its rear surface with the output of a continuous working (cw) CO_2 laser. Deposition times were in the range 1-45 mins. All substrate were cleaned with acetone prior to insertion into the reactive solutions used for hydrothermal growth of ZnO.

B. Hydrothermal Deposition.

0.1M solutions of zinc nitrate and HMT (Alfa Aesar, 99% and 99+%, respectively) in water (Elgastat, resistivity $> 18\text{m}\Omega\text{cm}$) were prepared and then maintained at 90°C in a thermostatically controlled oil bath for about 30 mins. For hydrothermal growth of ZnO, 50mL aliquots of each solution were mixed together in another glass bottle of maximum volume 130ml, the pre-heated substrate of interest was immediately immersed in this reaction solution, and the bottle was then sealed and heated at constant temperature (90°C), without stirring, throughout the growth process. Growth times, t , spanned the range 3-12h. NT formation on the tops of some of the initially formed rods was evident after $t \sim 6\text{h}$. The as-growth sample were cleaned by rinsing in deionized water, and then dried in air in a laboratory oven at 80°C .

C. Characterization.

The deposited products were characterized and analysed by scanning electron microscopy (SEM, JEOL 6300 LV), transmission electron microscopy (TEM, JEOL 1200EX), high-resolution TEM (HRTEM, JEOL 2010), and x-ray diffraction analysis (XRD, Bruker AxS D8 Advance Powder Diffractometer with $\text{CuK}\alpha$ radiation).

III. RESULTS AND DISCUSSION

D. Growth of ZnO Nanorods/Nanotubes on ZnO precoated substrates.

Synthesis of ZnO NRs on seeds have been reported previously [28,29]. In the present experiments, well aligned ZnO NRs could be obtained within $t \sim 3\text{h}$ when using Si substrate that had been precoated with a PLD ZnO template [32] once $t > 3\text{h}$, the morphologies of many of these NRs begin to evolve from hexagonal rods to “syringe” like structure [9].

Figure 1 a shows an SEM image of a ZnO sample grown for $t = 3\text{h}$ on a PLD ZnO-pre-coated Si substrate. When the growth continues for $t = 6\text{h}$ as shown in figure 1 b single (or in a few cases, multiple) “volcano-like” structure with a hole are evident on the tops of some of the longer rods; most of these volcano-like structures appear at or near the center of the precursor ZnO NR. Ultrathin ZnO NTs emerge from such structures at extended t . This is illustrated by the 30° tilt SEM image of a $t = 9\text{h}$ sample shown in figure 1c, in which well-aligned NTs are clearly evident. This SEM image shows the direction of NR. The NT length increases with t , as demonstrated by the SEM image of a $t = 12\text{h}$; sample presented in figure 1d. TEM images of material from the $t = 9\text{h}$ and 3h samples shown in figure 1e and f confirm the tabular and rodlike nature of these structures. The wall thickness of these NTs is typically 5-15nm, and their outer diameter, $d \sim 20\text{-}40\text{nm}$. Some nanowires with $d < 20\text{nm}$ are also formed in our experiments. There may be a minimum d below which a tabular structure cannot be supported. Figure 1g shows a HRTEM of the top of a single NT, exhibiting a wall thickness of $\sim 7\text{nm}$. Crystal planes aligned perpendicular to the growth directions is clearly visible. The measured inter-plane spacing (0.52nm) matches well with the literature value for planes such as (001) in wurtzite ZnO (lattice parameter = 0.5196nm) reinforcing the conclusion that the NTs grow along the (0001) direction. The accompanying SAED pattern shown in figure 1h serves to confirm the single-crystal nature of the ZnO NT sample. SEM images of

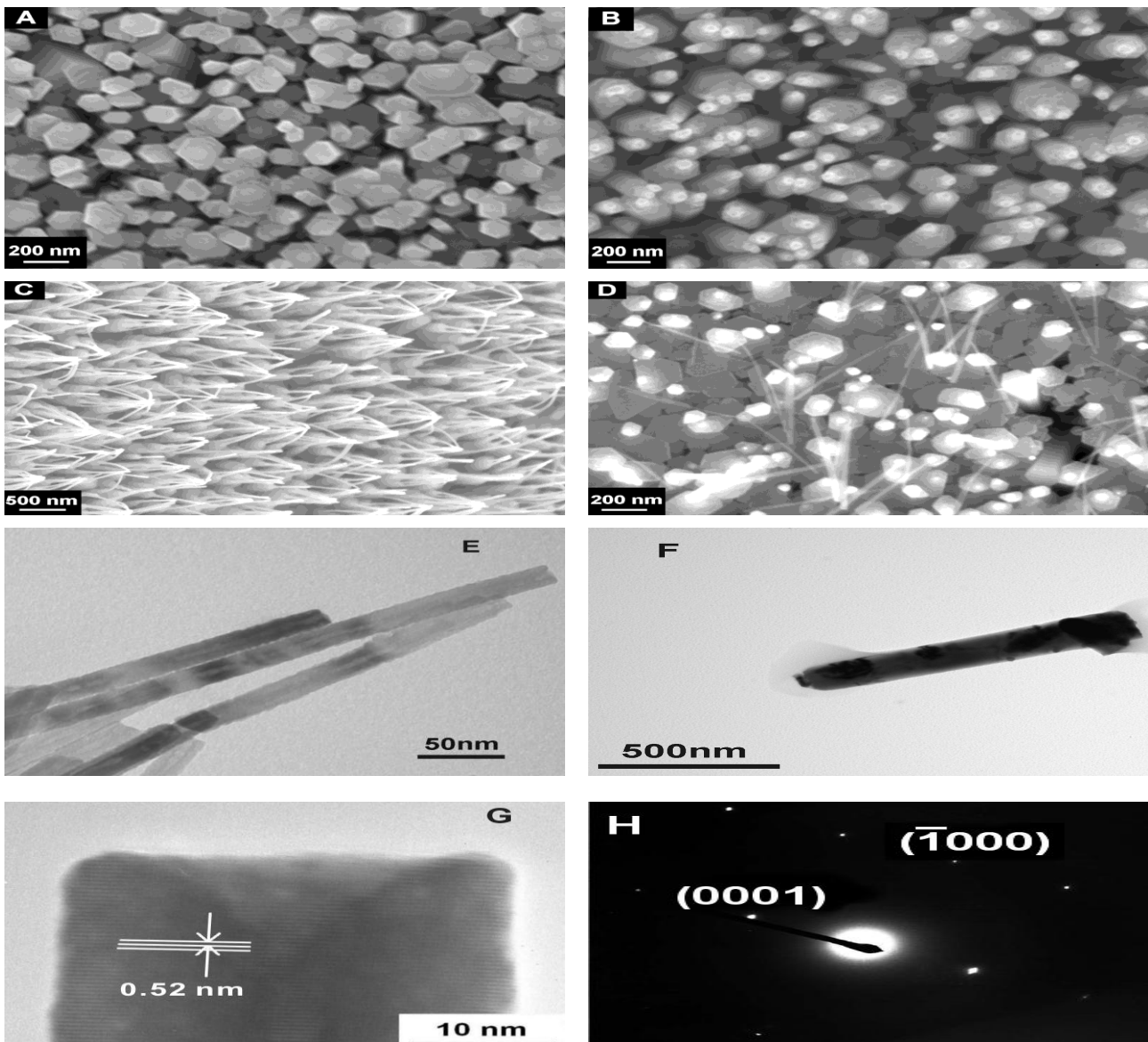
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ZnO nanorods grown directly on bare silicon substrate for $t = 3$ h, 6 h, 9 h and 12 h are shown in figures 1 I to L. Extending t beyond 6h appear to have little effect on the lengths, diameters or morphology of these NRs. All of the rods in images I to L appear as hexagonal columns with flat tops; their alignment is noticeably poorer than in case of the arrays grown on PLD ZnO-coated Si substrates. The samples grown in figure 1 I to L were also studied by TEM (with SAED) and by XRD. These analyses confirm that all of the products are single-crystal ZnO. Two conclusions can be drawn from these observations:

- i- Because the morphologies of the NRs grown on uncoated Si all mirror those of the NRs grown on PLD ZnO-coated substrates and the emergence of NTs are attributable to any fundamentally different morphology or structure of the precursor rods grown on the PLD ZnO-coated substrates.
- ii- NT formation is only observed in the case of samples in the case of samples grown on PLD ZnO-coated substrates, thus implying some key role for the ZnO template in the formation of tubular structures.



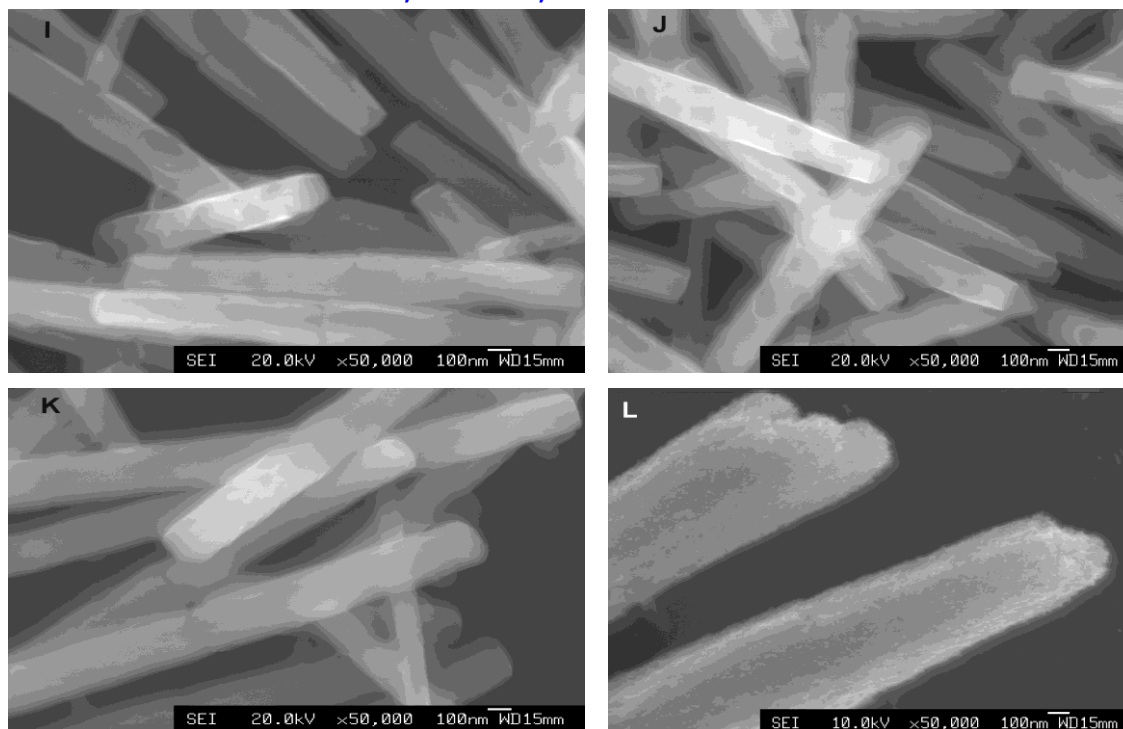


Fig.1: Electron microscope images of ZnO nanoarrays grown on silicon substrates pre-coated, using PLD, with ZnO seed layers. The ZnO was formed by the hydrothermal reaction of 50 mL 0.1 mol dm⁻³ Zn(NO₃)₂ and 50 ml 0.1 mol dm⁻³ HMT at 90 °C. Samples were removed from the reaction solution at different times. (A) a top view SEM image of a substrate removed from the reaction solution after 3 hours. (B) a top view SEM image of a substrate removed from the reaction solution after 6 hours. (C) a 30° tilt SEM image of a substrate removed from the reaction after 9 hours. (D) a top view SEM image of a substrate removed from the reaction solution after 12 hours. (E) a TEM image of the nanotube formed on the substrate after 9 hours. (F) a TEM image of nanorod formed on the substrate after 3 hours. (G) HRTEM of the sample from the top of an individual nanotube. (H) SAED pattern of the nanotube. (I), (J), (K) and (L) are top view SEM images of bare Si substrates removed from the reaction solution after 3, 6, 9 and 12 hours respectively.

E. Growth Properties of ZnO Nanorods/Nanotubes.

Hydrothermal growth of ZnO crystal with variable, yet controllable, morphologies has been reported widely [30-32].

The growth habit of ZnO is determined mainly by the structure of the crystal, but is also sensitive to a number of external conditions such as pH, the zinc source (and its counterion), the presence (or not) of any complexing agent, the nucleation condition (including effects due to the presence of a substrate) the extent of super-saturation, etc. The present hydrothermal growth studies were all conducted in sealed glass jars maintained at 90°C and without stirring. This is because the properties of the reactive solution, both bulk and in the immediate vicinity of any growing NR, will be time dependent, and the morphologies of ZnO crystal formed at early t may thus evolve through a range of dissolution/recrystallization phases during the full “growth” period.

F. Solution Effect.

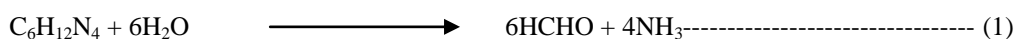
The concentrations of the various reactive species in the growth solution are a crucial factor in determining the product morphology. In-situ measurements of the variation in the pH value of the sealed reactive solution with growth time showed a sharp fall (from 5.34 to 5.20) in the first 10min, which gradually recovered to pH ~ 5.31 by t=2h and thereafter remained constant. Aliquots of solution were removed at regular intervals and the zinc ion concentration was determined via anodic stripping Voltammetry, performed using a Hg- plated polished glassy carbon electrode. The total zinc ion concentration decrease rapidly during the first 2h, mainly as a result of precipitation, then shows a slow, zeroth order decline from ~ 10 to ~ 2mM over the next 6h before settling at a long time value of ~ 1 mM (close to the current detection limit). Zn(OH)₂ [33-35] and Zn(OH)₄²⁻ ions [36-38] have been proposed as likely precursor species in the hydrothermal growth of ZnO crystals. Calculations based on standard enthalpy changes of formation and entropies

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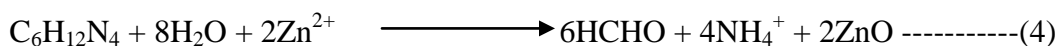
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of zinc aqueous and ammine complexes and zinc oxyanions indicate that at the recorded pH and temperature of these experiments, $Zn^{2+}(aq)$ will be the principal aqueous zinc species. The following reactions are important in the formation of ZnO NRs under such conditions:



Once all the hydroxide ions formed by the decomposition of HMT have reacted with the Zn^{2+} ions, the net reaction is



and the PH of the solution remains constant as shown in figure 2 below:

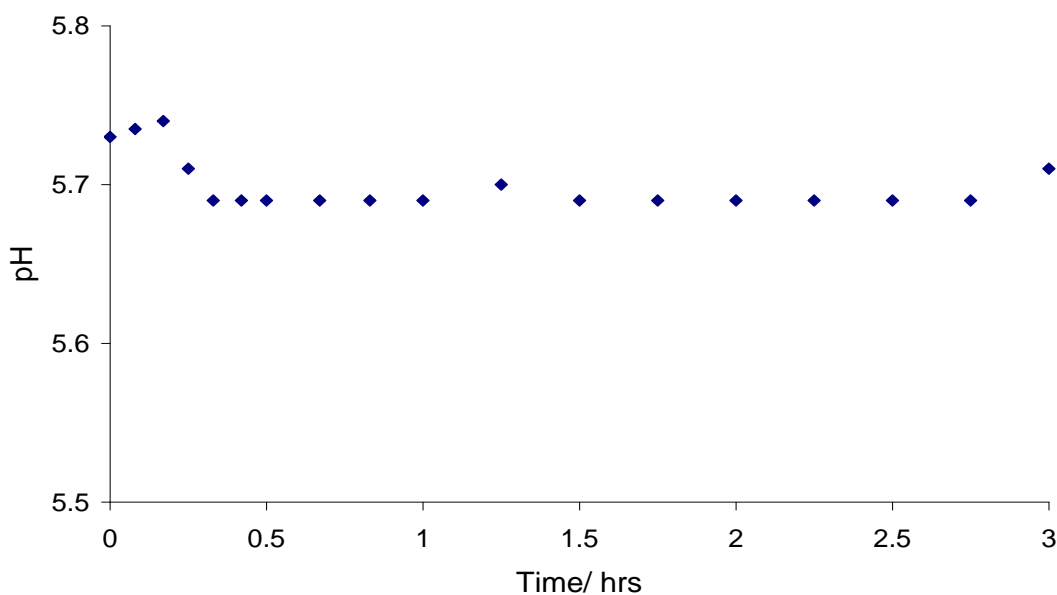


Fig. 2: pH profile obtained after mixing 50 mL 0.02 mol dm⁻³ zinc nitrate hexahydrate and 50 mL 0.02 mol dm⁻³ hexamethylenetetramine at 90 °C over 3 hours

Several groups have investigated controlling the ZnO product morphology by altering the composition of the reactive solution [39-41]. Zhang et al. [42] reported that the Zn^{2+}/OH^- ratio affects the morphologies of ZnO fibres, with low Zn^{2+}/OH^- ratios favouring growth of fibers, with large aspect ratios. The pH of the reactive solution used in the present experiments is constant after $t = 2h$, whereas, the Zn^{2+} concentration continues to fall. To investigate the effect of Zn^{2+}/OH^- ratio on the resulting NRs, standard reactive solutions were mixed and left to age for 9h prior to the introduction of PLD ZnO-coated Si substrates. The resulting deposits was analyzed after growth for $t = 9h$. SEM images of the sample (top and 30° tilt views) are shown in Figures 4 a and b. Figures 4 c and d shows the TEM and EDX spectrums confirming that the sample grown on the substrates are actually ZnO NTs and not artifacts in solution. The NR diameters decrease and the length/diameter aspect ratios increases as growth proceeds, that is, as the solution ages and the Zn^{2+}/OH^- ratio decreases giving rise to the observed nanotubes. The “Clumping” of the longer, thinner NTS in figure 4a and b is attributed to surface tension effects during the sample drying. This “Clumping” effect on the

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NTS was treated by employing the critical drying technique shown in figure 5 a and b. Figures 5 c and d shows the TEM and EDX spectrums confirming that the sample grown on the substrates are actually ZnO NTs and not artifacts in solution. Any eventual explanation for the two different classes of observed NR growth behavior should thus reflect some difference in the local solution (perhaps induced by the surface polarity. The role of HMT in the growth of ZnO nanostructures remains a matter of some debate. O' Brien and co-workers suggest that its primary role in the hydrothermal growth of ZnO is as a pH buffer [22]. Thus, HMT can act as a slow release source of OH⁻ ions (through reactions 1 and 2), consistent with the observed stable long term pH of the reactive solution in the present experiments. HMT, HCHO and NH₃ could all also adsorb on ZnO, with crystal plane specific efficiencies. Selective adsorption of any or all of these species could thus influence growth rate along different axes and thus the morphologies of any resulting ZnO crystal. This suggest that different local conditions at, or on the fastest growing surface of the ZnO crystal may be responsible for the two different classes of NR observed in the early growth stages and the selective evolution of one of these types into NTS at longer growth times.

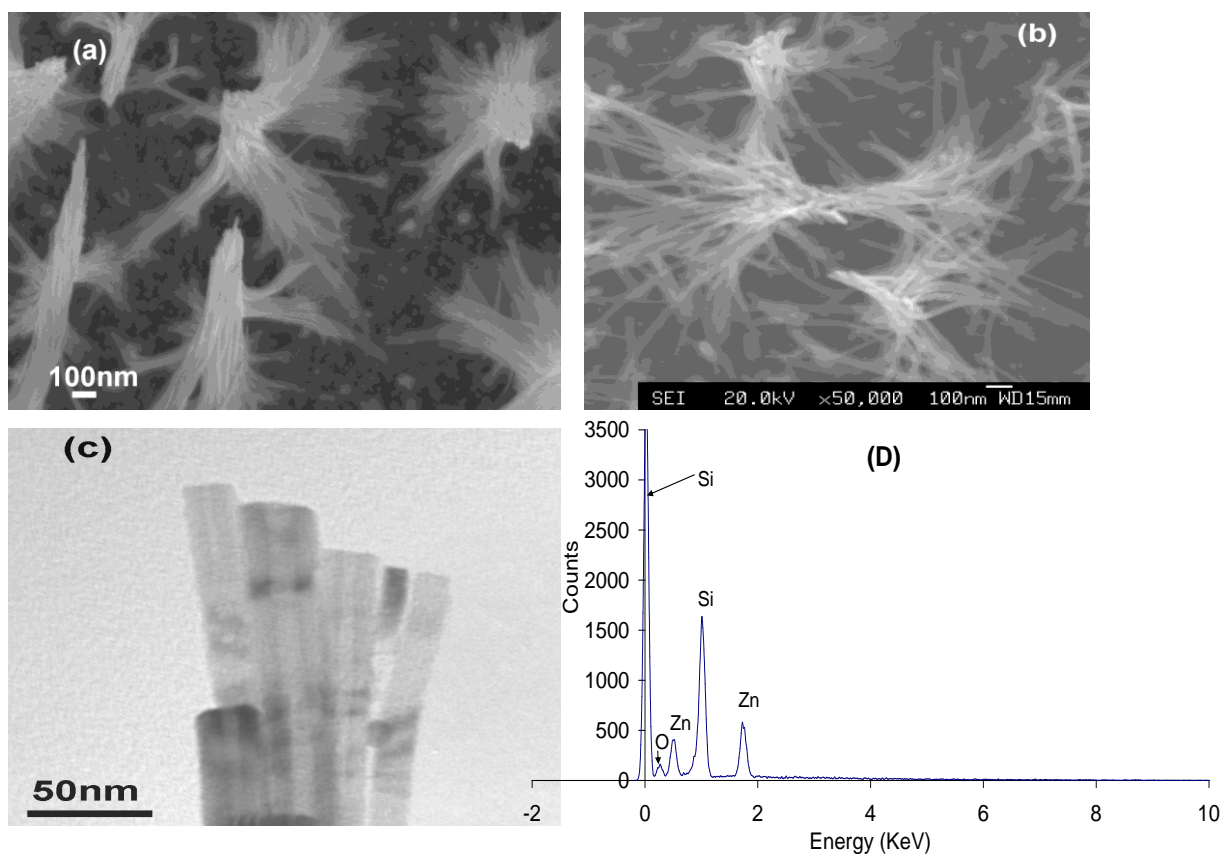


Fig. 4: Electron microscope images of ZnO nanotubes on silicon substrates pre-coated, using PLD, with ZnO seed layers. The ZnO nanotubes were formed by the hydrothermal reaction of 50 mL 0.002 mol dm⁻³ Zn(NO₃)₂ and 50 ml 0.002 mol dm⁻³ HMT at 90°C for 9 hours. (a) shows the top view SEM and (b) 30° tilt SEM image of the sample grown on the substrate respectively. (c) a TEM image of the nanotube formed on the substrate. (D) EDX spectrum confirming the sample grown on the substrate is ZnO nanotube.

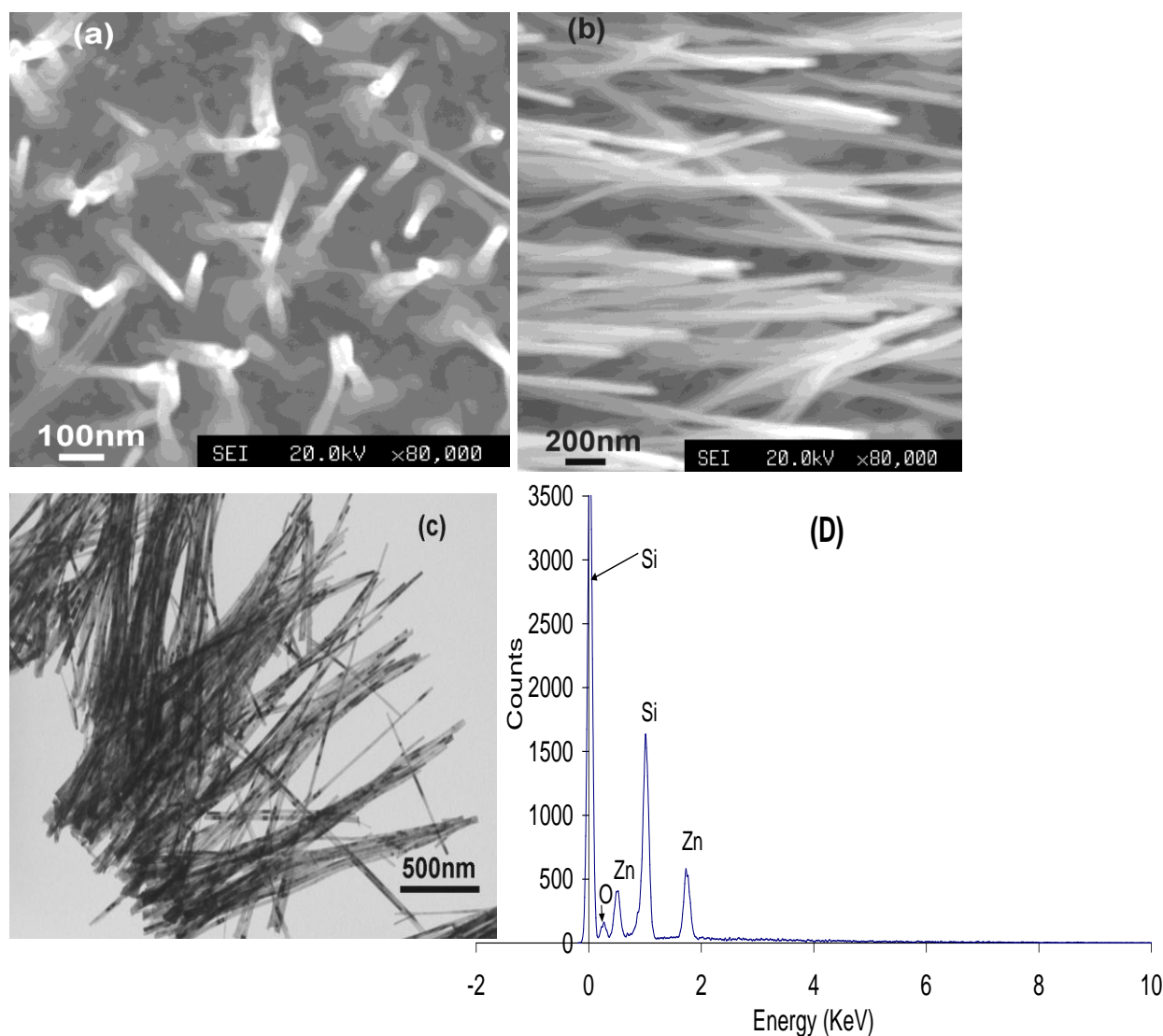


Figure 5: (a) and (b) top and tilt view SEM images and (c) TEM image of a sample grown for 9 hours that was post-treated by critical point drying. (D) shows the EDX spectrum of the sample. The reactive solution was prepared by mixing 50 cm³ aliquots of 0.002 mol dm⁻³Zn(NO₃)₂ and HMT.

IV. CONCLUSION

ZnO NRs have been synthesized on PLD ZnO film templates by hydrothermal growth in an equimolar mixture of aqueous zinc nitrate and HMT maintained at 90°C, without stirring, NTs were observed sprouting from the top of some of the longer NRs after extended growth times (when the total zinc concentration in solution was much depleted). HRTEM and SAED analysis confirms that these NTs are single crystal ZnO and that their growth direction is (0001). Ways in which the hydrothermal growth of both NRs and NTs depend on properties of the substrate and of the reactive solution have been investigated further. These show the PLD ZnO film to be a key factor in the appearance of NTs. The film provides a template of (preferentially c- axis aligned) nanocrystallites, which present Zn⁻ or O⁻ atom, terminated Zn-polar (0001) faces that serve to nucleate the subsequent hydrothermal growth of NRs. We propose that the electrostatic interactions induced by the former termination cause a local decrease (relative to the bulk) in the Zn²⁺/OH⁻ (and ZnOH⁺/OH⁻) concentration ratios in the immediate vicinity of the growing surface, which reduces the degree of

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solution super-saturation and favours tapered NR growth and as the zinc concentration falls further, the emergence volcano-like structures on the polar surface, which seed the subsequent growth of ZnO NTS and in certain cases, thin nanowires, such mechanistic studies of hydrothermal growth of ZnO in general and of ZnO NTS in particular serve to aid our understanding on the effect of polarity and surface termination on the growth habit of ZnO crystals, which in turn, is likely to assist the realization of controllable growth of ZnO nanostructures or a quality appropriate for nanodevice fabrication.

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