

Controlling The Growth Direction of ZnO Nanowires on *c*-Plane Sapphire

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ABSTRACT

Well oriented vertical ZnO nanowires (NWs) are grown on *c*-plane sapphire via a vapor-phase transport process using an Au thin film as a catalyst. This new finding is unexpected due to the fact that the lattice mismatch between the zinc oxide and the underlying substrate is 18%. X-ray diffraction (XRD) analysis shows that single-crystal, wurtzite NWs grow in the [0001] direction normal to the basal sapphire plane, which proves that *a*-plane sapphire is not essential for growth of vertical ZnO NWs, as has been previously stated.[1] We have found that by controlling the thickness of the Au-film and pre-growth annealing of the Au/sapphire substrate NWs can be grown either tilted or vertical. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) studies on Au films with thicknesses ranging from 1 to 10 nm show that in the absence of film annealing, NWs can be grown 32° tilted from the surface normal, whereas pre-annealed Au films result in growth of NWs in the surface normal direction. We attribute the formation of the normal and tilted growth directions to the surface concentration of O and Al ions on sapphire.

INTRODUCTION

In the past two years there has been a renewal of interest in ZnO sparked in part by the reports on synthesis of ZnO NWs as quasi one-dimensional materials [1] and by their potential applications as blue light emitters, electron field emitters and sensors. Due to its wide band gap (3.37eV) and large exciton binding energy ZnO is an excellent alternative to the UV and blue-green GaN-based light sources. [2] In general, in designing NW-based light emitting devices, there are fabrication issues such as controlling the doping level of NWs, ideal connection of NWs to the conducting electrodes and the geometry of NWs in the device that ought to be addressed in order to have an efficient device. This study focuses on the latter issue. Our goal is to control the growth direction of ZnO NWs on sapphire and other suitable substrates to prepare arrays of NWs with preferred orientation.

c-plane sapphire (0001) has been the most popular substrate in the epitaxial growth of III-V and II-VI semiconductors due to its high crystalline perfection, stability at high temperature and transparency. The growth of ZnO films on this substrate is accompanied by a large number of defects at the substrate/film interface, which in part is due to the significant lattice mismatch between ZnO ($a = 3.2495 \text{ \AA}$, $c = 5.2069 \text{ \AA}$) and sapphire ($a = 4.758 \text{ \AA}$, $c = 12.990 \text{ \AA}$). [3, 4] In device fabrication, this mismatch is significant and ultimately results in lower charge mobility, defect related carrier concentrations [3] and has been one major obstacle to the use of ZnO films. Recently, Fons *et al.* [4] have reported that ZnO films can be grown on *a*-plane sapphire with lower defect density relative to those on the *c*- plane. This was mainly attributed to the fact that the *a* and *c* lattice parameters of ZnO and sapphire (respectively) are related by a factor of ~ four. Not surprisingly and perhaps stimulated by the work of Fons' *et al.*, all the reports on epitaxial

fabrication of ZnO NWs on sapphire have been carried out on *a*-plane sapphire. These reports include standing ZnO NWs by Huang et al, [1] tilted ZnO NWs by Ng et al, [5] “tower-like” ZnO structures by Hu et al [6] and NWs grown on nanowalls. In the present work, NWs are grown on *c*-plane sapphire substrates coated with Au films with thicknesses ranging from 1 to 10 nm. The impact of film thickness and thermal annealing of these films on NWs growth direction are studied and conditions for controlling the morphology of the NWs are presented.

EXPERIMENTAL

Standard one-side polished *c*-sapphire wafers cut into pieces (3 mm²) were coated with different Au thicknesses, 1 nm to 8 nm, using a thermal evaporator. Au film annealing was performed at 900 °C for 10 minutes with a ramping rate of 97 °C/min. The tube furnace was purged with ultra-pure Ar prior to annealing at room temperature and during annealing. Similar amounts of zinc oxide (99.999% purity) and graphite (99.99% purity) were ground (total mixture weight of 0.1 g) and in a Si boat transferred to the center of a small quartz tube (12 cm length, 2 cm diameter). The quartz tube was then placed inside a tube furnace (80 cm length, 5 cm diameter), such that the center of the boat was at the center of the furnace. The Au-coated sapphire substrates were placed 6 cm downstream from the center of the tube. The tube furnace was purged with Ar (0.50 L/min.) for 15 minutes at room temperature, then the temperature was increased to 900 °C (at a rate of 109 °C/min) and kept constant for 20 minutes under a flow of Ar gas. The nanostructures were imaged by SEM at 1-5 kV. The crystalline quality of the ZnO NWs was assessed by X-ray diffraction (XRD) using a standard diffractometer with Cu K α radiation in the θ -2 θ configuration.

RESULTS AND DISCUSSION

Systematic studies were carried out that detail the effects of Au thickness and Au film morphology (unannealed vs. annealed) on the growth and orientation of ZnO NWs on *c*-plane sapphire. Growing NWs on substrates coated with as deposited unannealed Au films with thicknesses ranging from 1 nm to 10 nm results in an interdigitated structure of NWs as shown in Figure 1.

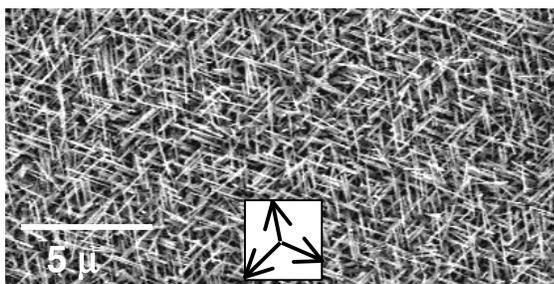


Figure 1: Tilted NWs grown on as deposited Au film composed of features with heights ranging from 1 to 10 nm. The inset shows the three unique growth directions.

In this structure NWs in addition to the normal direction, grow in six different directions with a symmetry of C₃ (inset of Fig. 1). In Figure 2a and 2b, a close-up view of the edge of this structure shows that at the border of the film, NWs grow normal to the surface, while at the

film's center the number of tilted NWs increases. XRD of this sample (Fig. 2c) shows two intense ZnO reflections, (0002) ($I=100\%$) and $(10\bar{1}1)$ ($I=82\%$). The angle between the (0002) and $(10\bar{1}1)$ crystallographic planes is 31.97° (in the wurtzite structure), which translates into a 58.03° tilt of $[10\bar{1}1]$ direction relative to the substrate basal plane. This angle is in close agreement with, the tilt angle of NWs, which from SEM images was found to be $55\pm 3^\circ$. As a result the (0002) reflections on the XRD scan are assigned to vertically oriented NWs, while $(10\bar{1}1)$ reflections are assigned to tilted NWs. In the tilted NWs, the $(10\bar{1}1)$ planes are parallel to the substrate surface and the growth direction is $[0001]$.

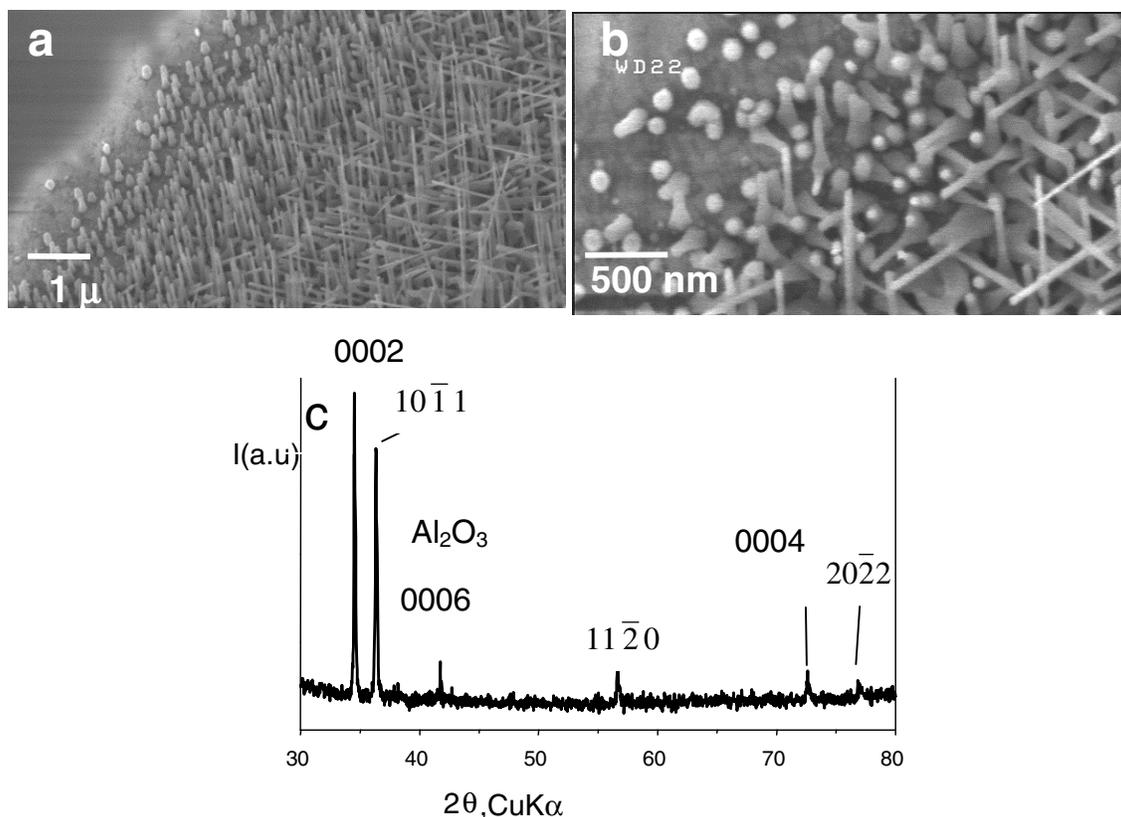


Figure 2: a) The side and b) the top views. In parts (a and b), it can be seen that the smaller Au droplets at the outmost part of the film grow normal, while moving towards the center of the film, tilted NWs grow. c) XRD pattern of the vertical and tilted NWs shows two intense ZnO reflections, (0002) and $10\bar{1}1$. The (0002) reflection is attributed to the vertical NWs and the $(10\bar{1}1)$ reflection to the tilted ones. Weak $(11\bar{2}0)$ reflection indicates presence of very small amount of ZnO NWs with c-axis parallel to the substrate surface.

The XRD pattern in Figure 2c also shows the presence of a weak $(11\bar{2}0)$ reflection, which suggests that some of the NWs are laying flat on the substrate. Note that in these experiments, the interdigitated NWs were obtained for all unannealed Au films regardless of their film thickness. Next, we tested the effects of annealing of the Au thin films, again 1 to 10 nm series, on the growth and orientation of ZnO NWs. It is found that annealing at 900°C (in

Argon) prior to ZnO growth promotes the vertical growth of the ZnO NWs on *c*-plane sapphire (Figures 3a and 3b).

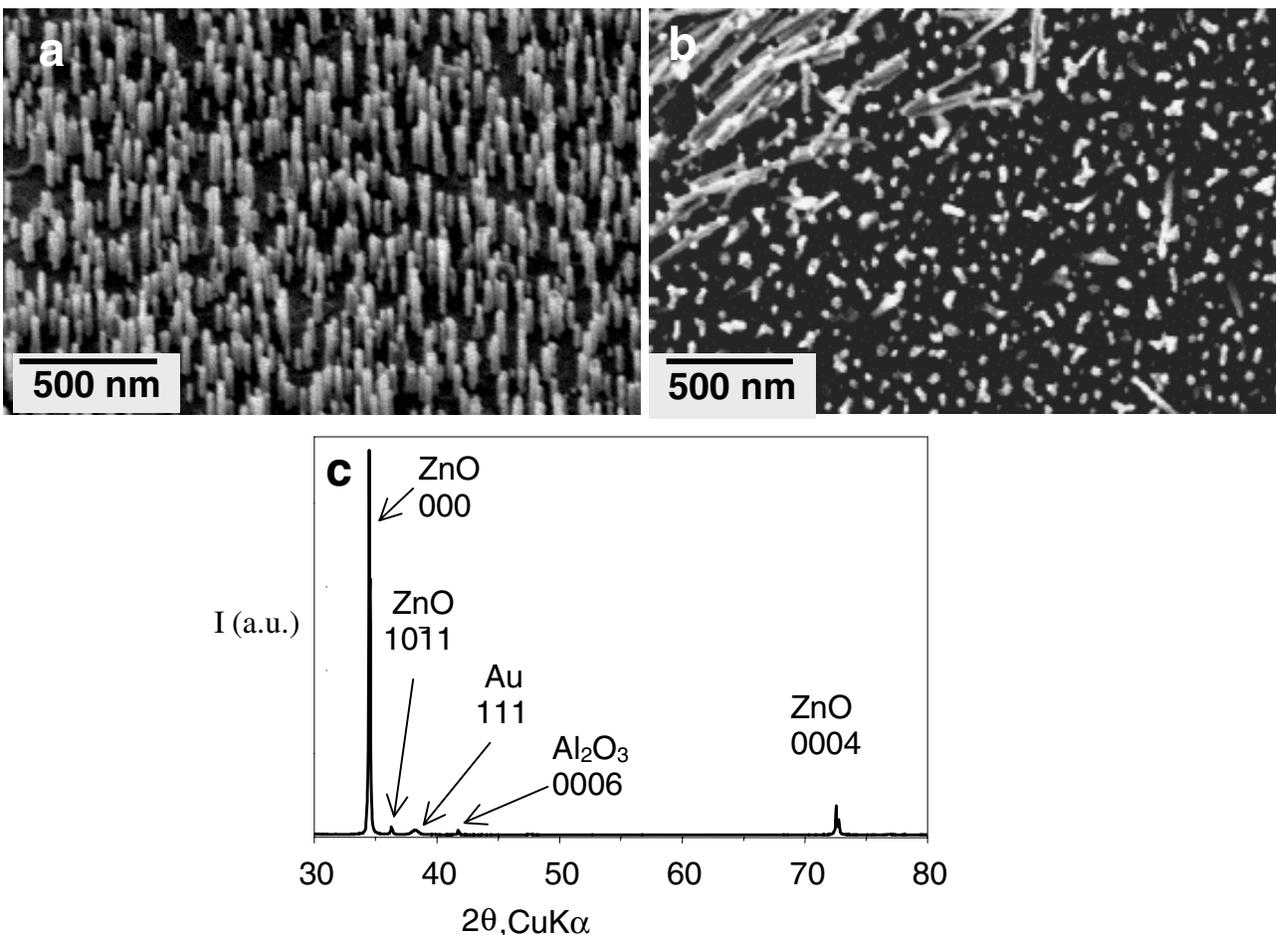
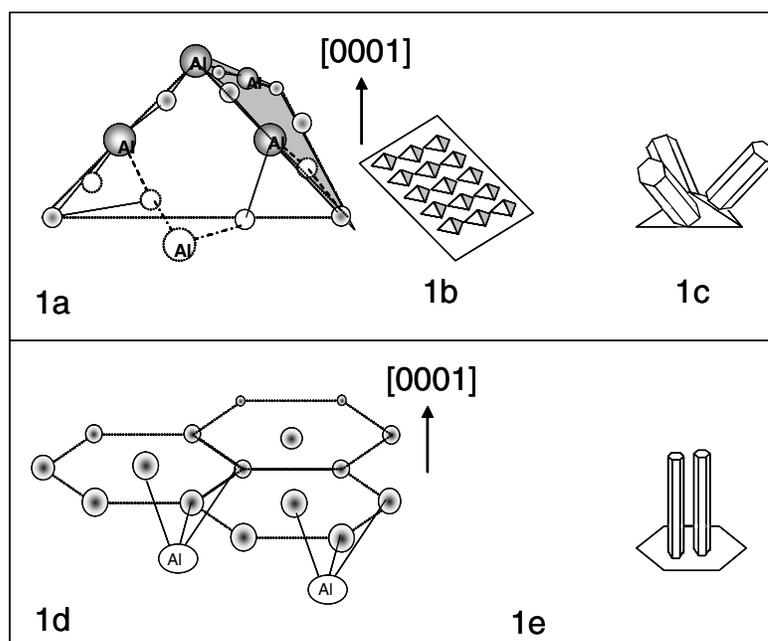


Figure 3: a) Standing ZnO NWs grown on *c*-plane sapphire viewed at angle and b) from top. c) XRD pattern of standing NWs. The strong (0002) and (0004) reflections are indicative that NWs are well oriented and grow in the *c* direction.

The XRD pattern of vertical ZnO NWs is shown in Figure 3c and illustrates that by pre-annealing the Au film, the intensity of the ZnO (10 $\bar{1}$ 1) reflection becomes less than 2% of that of (0002). This indicates that nearly all ZnO NWs are single-crystalline and oriented in the [0001]_{hex} direction normal to the substrate surface. The *c*-lattice parameter of ZnO as calculated from the positions of the (0002) reflections is $c=5.2071(5)$ Å, which correlates well with the *c*-value of 5.2069 Å for bulk ZnO. NWs thickness measurements using AFM shows that the diameter of both tilted and vertical NWs are similar and is between 30-80 nm. Annealing Au films thicker than 6 ± 2 nm resulted in the growth of vertical NWs on a network of ZnO bridges (not shown here). It is not clear why in the absence of Au annealing NWs grow tilted and whether the substrate plays a role in dictating the growth direction of NWs. Answering these questions becomes further complicated by the large lattice mismatch between ZnO and sapphire.

It is likely that the surface smoothness and the surface termination of the substrate are among the factors that can be influenced by annealing the Au coated sapphire substrate. Annealing sapphire at high temperature (1000-1400 °C) has been found to form ultra-smooth surfaces because of surface atom reconstruction. [7] For the Au coated sapphire, however, the extent of surface smoothness is not clear and might not be significant due to the lower annealing temperature (900 °C). The other possibility is associated with the nature of the surface and its alteration upon annealing. To examine the role that the sapphire substrate plays on the growth direction, NWs were grown on *a*-plane (110) sapphire with similar experimental conditions as to that of the *c*-plane. In this case NWs tilted in 4 different directions, rather than the six directions observed on *c*-plane sapphire. This shows that the arrangement of atoms on the (110) plane does have impact on the growth direction. Thus change in the NW growth direction upon annealing can be a result of a change in the surface structure of the substrate relative to the unannealed surface. We think that the observed growth directions in the absence and the presence of annealing are mainly dictated by the surface termination of the sapphire substrate. In our hypothesis we assume that in the absence of annealing the sapphire surface is mostly terminated with Al ions. This surface is shown in scheme 1a in which each Al ion on the surface is connected to three oxygen ions of the underneath layer. [8] The symmetry of the terminal Al-O on the surface matches very well with that of the growth direction of the NWs (Schemes 1a, 1b, 1c and Fig. 1). Note that the size of the facets in scheme 1a is not realistic, and the motive is to show the position of Al atoms on an Al terminated surface. Further analysis is required to validate this model.



Scheme 1: a, b) Illustrates Al-terminated sapphire in the [0001] direction. Oxygen ions are not labeled. Al-O symmetry on the surface matches exactly with the NWs growth directions. d) by removing Al ions from the surface in scheme 1a, an O-terminated surface can be pictured. In this case, the O ions are coplanar and their hexagonal symmetry matches with that of the attached Zn ions. 1e) vertical NW growth is seen in the case of surface rich oxygen substrates, which agrees with the proposed surface in 1d.

In the case of the annealed Au film on sapphire, it is assumed that the surface is mostly covered with O ions. Results show that after annealing a clean sapphire surface, the surface becomes hydrophilic, which is good evidence of an increase in the surface coverage of the O ions on the surface. As shown in scheme 1d, the O ions are coplanar and have hexagonal symmetry; this is similar to the symmetry of Zn ions in ZnO along the [0001] direction. Scheme 1d shows an O-terminated sapphire plane and its orientation relative to the [0001] direction. The observed normal growth direction of NWs after annealing matches nicely with the proposed scheme (1e). Electron-back-scattered diffraction (EBSD) and high-resolution cross-section microscopy (TEM) analysis are underway which will aid in the determination of the microstructure of these NWs and their crystallographic relationship with the c-plane sapphire substrate.

In conclusion, controlling the growth direction of ZnO NWs on c-plane sapphire is demonstrated. The impact of Au film thickness and film annealing on the produced nanostructures are evaluated. We show that by pre-annealing the Au film (ranging from 1 to 10 nm) it is possible to grow vertical NWs rather than tilted ones. This is the first example of vertically aligned ZnO NWs with their *c* axis parallel to that of the sapphire substrate. A preliminary model is proposed in which the vertical and tilted growth directions are facilitated on O-terminated and Al-terminated surfaces, respectively. The substrate surface termination /smoothness and crystal structure of the NWs at their interface with substrate are among the key factors in device fabrication and performance, which have not been studied systematically yet. Further study is essential to understand fully these relationships and to investigate whether such relationships hold between other materials.

REFERENCES

1. M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *Science* **292**, 1897 (2001).
2. R. D. Vispute, V. Talyansky, Z. Trajanovic, S. Choopun, M. Downes, R.P. Sharma, T. Venkatesan, M. C. Wood, R. T. Lareau, K. A. Jones, A. A. Iliadis, *Appl. Phys. Lett.* **70**, 2735(1997).
3. I. Ohkubo, A. Ohtomo, T. Ohnishi, Y. Mastumoto, H. Koinuma, M. Kawasaki, *Surf. Sci.* **443**, L1043 (1999).
4. P. Fons, K. Iwata, A. Yamada, K. Matsubara, S. Niki, K. Nakahara, T. Tanabe, H. Takasu, *App. Phys. Lett.* **77**, 1801 (2000).
5. H. T. Ng, B. Chen, J. Li, J. Han, M. Meyyappan, J. Wu, S. X. Li, E. E. Haller, *App. Phys. Lett.* **82**, 2023 (2003).
6. P. Hu, Y. Liu, X. Wang, L. Fu, D. Zhu, *Chem. Commun.* 1304 (2003).
7. M. Yoshimoto, T. Maeda, T. Ohnishi, H. Koinuma, O. Ishiyama, M. Shinohara, M. Kubo, R. Miura, A. Miyamoto, *Appl. Phys. Lett.* **67**, 2615 (1995).
8. V. E. Henrich, P. A. Cox, *The Surface Science of Metal Oxides*, (Cambridge University Press, New York, 1994) p. 53.