Hydrothermal Synthesis of Zinc Oxide Nanowires on Kevlar using ALD and Sputtered ZnO Seed Layers

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ABSTRACT

Low temperature hydrothermal methods allow for growth of nanowires on novel substrates. We examine the impact of variations in chemical concentration, time, temperature, and seed layer on nanowire (NW) growth and crystallite formation. The majority of growth (NWs and crystallites) was found to occur within the first two hours. Lower $Zn(NO_3)_2$ concentrations produced a reduction in the undesired large crystallites, whereas hexamethylene tetramine (HMT) concentration did not largely impact crystallite density or nanowire morphology. Growth temperature appeared to impact NW diameter variation. Nanowires grow only on the ZnO seed layer and crystallites seem to attach preferentially to the bare Kevlar surface.

INTRODUCTION

Recent work by Wang, *et al*. showed that ZnO nanowire (NW) coated Kevlar fibers can be mechanically actuated to produce small amounts of current, suggesting the possibility nano-piezo energy harvesting [1 – 9]. This application requires the uniform growth of NWs on novel substrates such as Kevlar. Due to the low decomposition temperature of Kevlar (~ 400 C), potential growth processes are limited to low temperature hydrothermal methods [10, 11]. To achieve selective growth of ZnO NWs on Kevlar, we used a uniform coating of ZnO to seed growth [12, 13], rather than the more widely used metal catalyst method [14]. An initial investigation of hydrothermally grown ZnO NWs on atomic layer deposition (ALD) and RF sputtered seed layers revealed the formation of large crystallites that could degrade the performance and reliability of piezoelectric nanogenerators. Since these large crystallites could not be removed easily without damaging the substrate or nanowires, the impact of growth parameter variation on prevention of large crystallite nucleation and growth was investigated.

EXPERIMENTAL DETAILS

The growth substrate used in these experiments is Kevlar 129, an aramid synthetic fiber. Two or more NW coated Kevlar fibers can be wound together as described in [1] so that if fibers are mechanically actuated, the NW coating may produce a piezoelectric current. Since the substrate is cylindrical, deposition of a uniform seed layer is more difficult than with a flat substrate. Because of its inherent high conformality, ALD was chosen as a seed deposition method. As an alternative, RF sputtering was also investigated; however, rotation of the fiber would be required for complete radial coverage. ALD seed layers were deposited using

$(C_2H_5)_2Zn$ and H_2O at 170 C. RF sputtering was performed using a ZnO target at 75 W and 10 mTorr. With both methods the target thickness of the seed layer was 100 nm. Prior to seed deposition, fibers were cleaned in DI water in a Branson 1200 bath sonicator for 60 seconds and then dried in a Blue M OV-8A gravity oven for 10 minutes at 80 C. A post growth rinse was not included because DI water can dissolve ZnO [15] and acetone and ethanol can change the Kevlar morphology [16].

Hydrothermal growth was conducted using $Zn(NO_3)_2$ and HMT. The $Zn(NO_3)_2$ dissociates in the DI water solution to form free Zn^{2+}. HMT breaks down to form formaldehyde (HCHO) and ammonia (NH_3) and is thought to increase local pH and coordinate to zinc to reduce free Zn^{2+} [17]. The reactions can be found in [18] and [19].

Nominal growth parameters used were 0.19 g $Zn(NO_3)_2$, 0.09 g HMT, 250 mL DI water, 80 C and a 6 h growth time. Growths were performed using a hot plate. A covered beaker was used to limit evaporation.

Scanning electron microscope (SEM) imaging was performed using an FEI Sirion XL30S-2 and a Leo 1560 with an accelerating voltage of 3.00 kV or 5.00 kV with a working distance in the range of 3 – 8 mm. X-ray diffraction (XRD) analysis of seed layers on Si was performed using a Bruker D8 Discovery.

EXPERIMENTAL RESULTS AND DISCUSSION

The impact of independent variation of $Zn(NO_3)_2$ concentration, HMT concentration, growth time, temperature, and seed layer on NW morphology and crystallite density is discussed.

$Zn(NO_3)_2$ Concentration Variation

The SEM images in figure 1 reveal the presence of large crystallites in addition to uniform NW growth on the surface of a Kevlar strand. These crystallites may be the result of exceeding the minimum critical supersaturation concentration of Zn for homogeneous nucleation in solution or for heterogeneous nucleation on surfaces other than the Kevlar substrate. In an attempt to reduce crystallite formation, $Zn(NO_3)_2$ concentration was varied around the nominal concentration of 0.19 g in 250 mL DI water to 0.28 g, 0.1 g and 0.05 g. The SEM images in figure 2 show that decreased $Zn(NO_3)_2$ concentration (0.1 g) appears to reduce solution phase precipitation of large crystallites without affecting NW density and morphology. Similar results were observed for 0.05 g (not shown). Further reduction of $Zn(NO_3)_2$ may result in a further decrease of the larger crystallites.

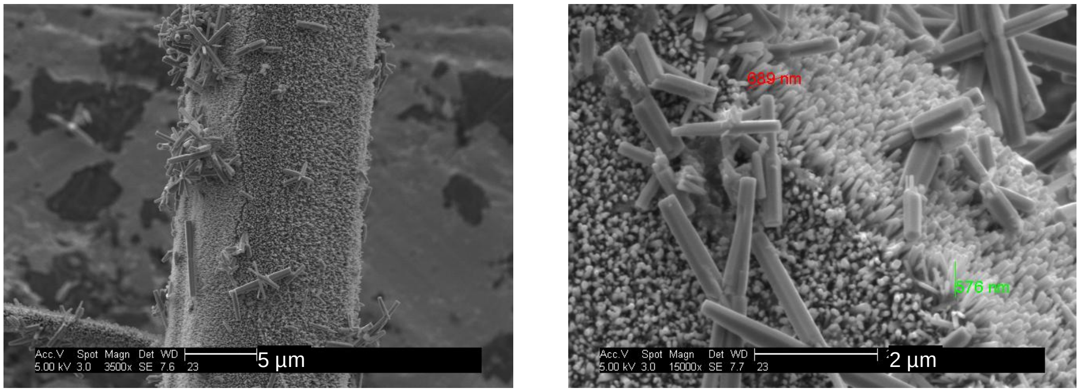

Figure 1. SEM images from growth with 0.19 g $Zn(NO_3)_2$, 6 h, 80 C.

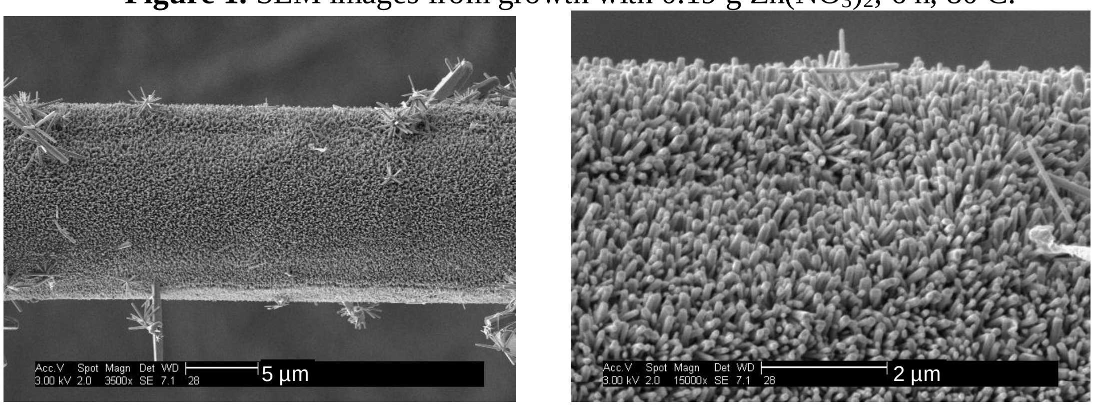

Figure 2. SEM images at from growth with 0.1g $Zn(NO_3)_2$, 6 h, 80 C.

HMT Concentration Variation

HMT is thought to locally increase pH and assist in nanowire formation [17]. HMT concentration was varied independently from 0.05 g to 0.19 g with all other parameters held at nominal values. Changes in HMT concentration did not cause clear changes in nanowire morphology or precipitate formation. Since no variation in nanowire growth is seen with the different HMT concentrations, a lower concentration may be sufficient to promote growth.

Growth Time Variation

Growths were performed for 2, 4 and 6 hours. No noticeable difference in nanowire morphology or crystallite density was observed, suggesting that the majority of nucleation and growth of NWs and large crystallites occurs within the first two hours consistent with [20]. This implies that growth times shorter than those used in [1, 21] can yield nanowires.

Temperature Variation

As shown in the SEM images in figure 3, a lower growth temperature of 70 C resulted in a larger variation in nanowire diameter in comparison to the nominal growth temperature of 80 C, but otherwise did not appear to strongly impact large crystallite density.

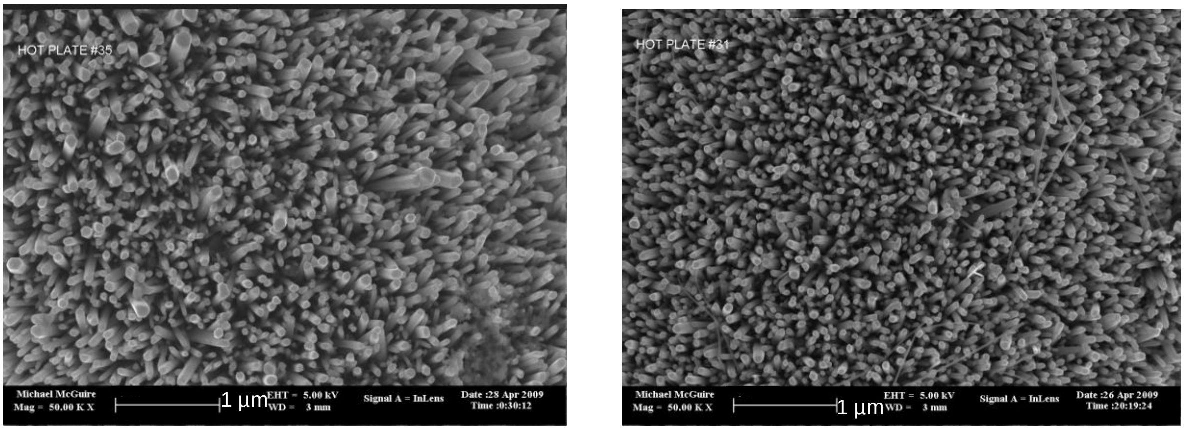

Figure 3. Comparison between 70 C (left) and 80 C (right) growth temperatures.

<u>Seed Layer Impact</u>

100 nm seed layers were deposited using ALD and RF sputtering. XRD data (figure 4) shows a distinct difference in seed layer crystallinity and orientation between ALD and sputtered ZnO seed layers on Si. Although this variation could be expected to impact wire orientation and morphology, a strong impact was not observed. SEM images in figure 5 show NW growth at nominal conditions on an ALD seed layer. As compared to figure 1, the ALD seed layer appears to produce less uniform nucleation and lower nanowire growth density. Higher magnification reveals that the NWs appear more tapered, which may not be a direct result of the seed layer. One possible explanation is ZnO etching and redeposition [19].

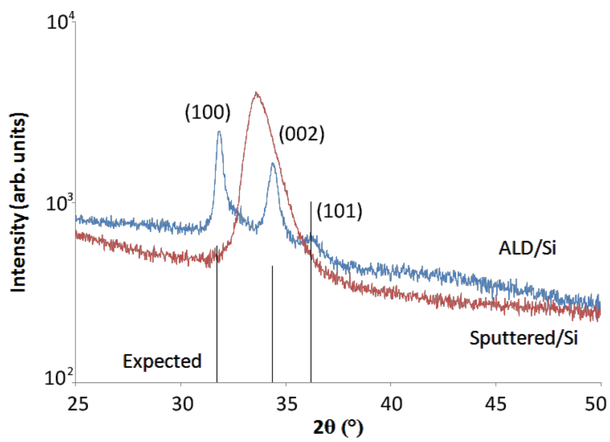

Figure 4. XRD scans of ALD and RF sputtered seed layers.

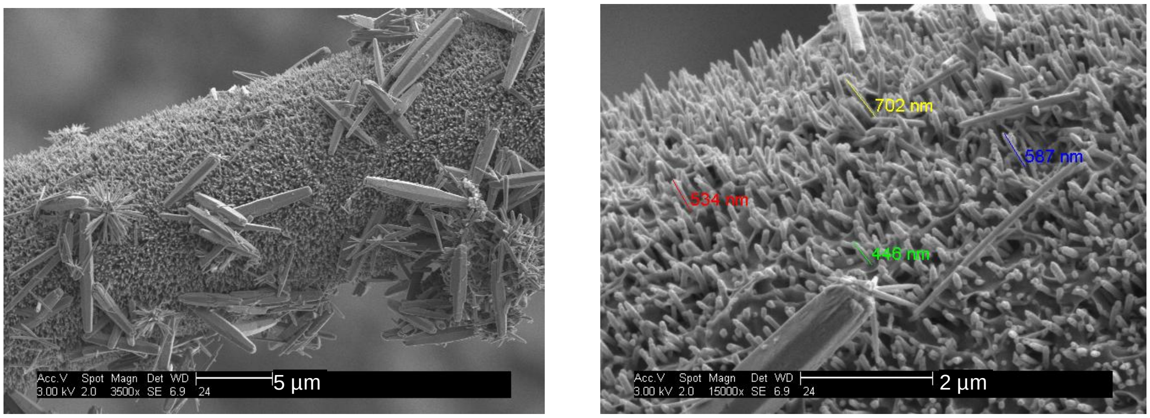

Figure 5. SEM images of ALD seed sample at nominal parameter settings.

The large crystallites appear to adhere more favorably to regions on the Kevlar surfaces lacking a ZnO seed layer. As shown in figure 6, many crystallites have collected on the left side of the image where the RF sputtered ZnO seed layer was shadowed (NW growth is absent), whereas the seeded (right) side is nearly crystallite free and shows uniform growth of ZnO NWs. Figure 7 shows that it is possible to produce large areas of uniform NW growth that are nearly crystallite free.

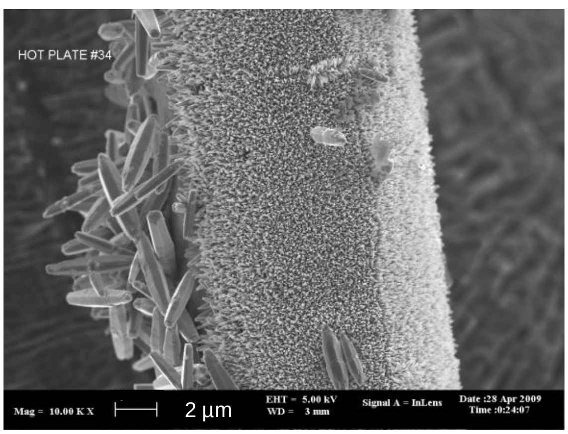

Figure 6. SEM image of growth patterns.

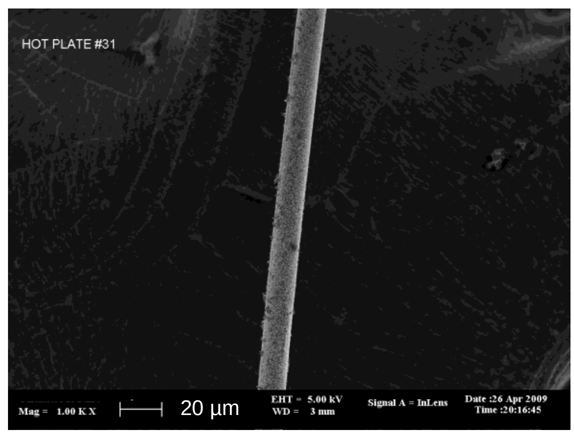

Figure 7. SEM image of uniform coverage.

Figure 8 shows cracking and separation of the seed layer from the Kevlar. NWs can be seen growing down from the separated seed layer and no NWs are seen where the seed layer was removed. These areas are denoted with arrows. Cracking and separation would limit the conduction of the seed layer and the ability to generate piezoelectric currents.

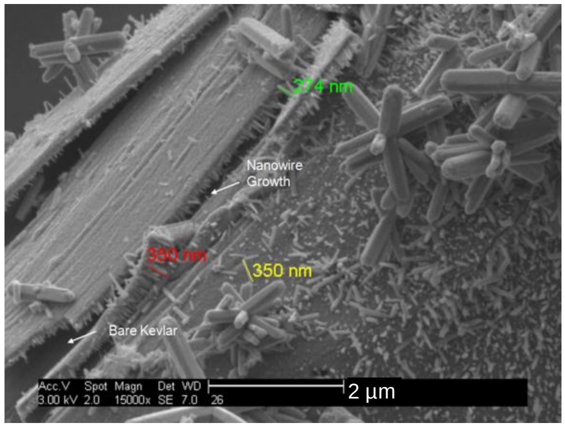

Figure 8. SEM image showing separation.

SUMMARY

The appearance of large crystallites during hydrothermal NW growth on Kevlar substrates may interfere with energy harvesting applications. A systematic investigation of growth parameters revealed that reducing $Zn(NO_3)_2$ concentration was the most effective method to decrease the number of these crystals. Changing HMT concentration did not appear to affect nanowire morphology or crystallite nucleation. A lower growth temperature led to larger nanowire diameter variation. Growth of NWs and crystallites appeared to saturate in less than two hours. Although differences in seed layer crystal structure were found in XRD results, the effects on NW morphology were not obvious. Nucleation seemed to be sparser on the ALD seed layer than on a sputtered seed of the same thickness. NW growth is shown on the seed layer and not on the Kevlar itself confirming that a ZnO seed layer is needed to nucleate growth. On the contrary, the large crystallites appeared to rest preferentially on the bare Kevlar surface. Further optimization to continue the reduction of larger crystals is underway.

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