PURELY SONOCHEMICAL ROUTE FOR ORIENTED ZINC OXIDE NANOWIRE GROWTH ON ARBITRARY SUBSTRATE

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ABSTRACT

We report a simple sonochemical method for the seeding and synthesis of Zinc Oxide nanowire arrays that can be formed on a number of substrates that are stable in alcohol and aqueous solution. Vertically aligned ZnO NWs were synthesized from a single solution at room-ambient via ultrasonic excitation. Prior to the NW growth, a ZnO seed layer was deposited using the same system with a different solution. The optimal conditions to produce a high density of oriented wires along with their optical characteristics are presented for ZnO NWs with a significantly high growth rate compared with traditional growth techniques such as evaporation, chemical vapor deposition and sputtering. Our method promises a mass-manufacturable process for fast and inexpensive ZnO NW production for practical low cost electronics, photonics and energy conversion applications.

Keywords: Zinc oxide, nanowires, sonochemistry, ultrasound, solution growth.

1.0 INTRODUCTION

Zinc Oxide (ZnO), a wide bandgap (3.37 eV) semiconductor with large exciton binding energy, and high visible light transmittance, has drawn considerable interest from a variety of disciplines including engineering, material science, and the biosciences. Attractive optoelectronic properties make it a good candidate for applications in solar cells[1], photodetectors[2], and displays. Its piezoelectric effect has also generated considerable interest for energy scavenging.[3] For practical low cost nanoelectronic applications, it is important to develop mass-manufacturable processes for fast and inexpensive ZnO nanowire production. Vertically aligned ZnO nanowires (NWs) have been produced on relatively short timescales by sonication[4-5], but this method requires costly Zn substrates or the deposition of Zn thin films to serve as a seed layer. Due to the low vapor pressure of Zn, deposition of this material would require a dedicated deposition system, which is not practical or cost effective in many cases. Although vapor-phase synthesis methods produce highly crystalline ZnO NWs, they require high temperatures which place limitations on acceptable substrates and the potential for device integration. Unlike the vapor-phase synthesis method, the hydrothermal method of growing ZnO NWs can be performed at much lower temperatures. The reaction time required for this synthesis of ZnO NWs however can take several hours (or even days). In this report, we propose a method proceeding at room ambient in less time, and using only one system (750W ultrasonic processor, Sonics and Materials). Using the method in this report, a continuous seed-layer deposition as well as an array of ZnO NW growth from the seed-layer is produced in a relatively short time and on various substrates over large areas. This

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technique was found to be advantageous from the viewpoint of environmental impact, scalability, process time, and production cost in comparison with other techniques.[6-8]

1.1 EXPERIMENTAL

The seeding process and growth were performed as follows. (I) A Si <111> substrate (9-15Ω.cm) was immersed in a solution of isopropyl alcohol and 0.005M zinc acetate dihydrate (C4H10O6Zn, 98+%). The solution was sonicated for 15 minutes at an intensity of 19W.cm^{-2} (1.3cm horn diameter) at 20 kHz. The process was repeated once to ensure a continuous layer of ZnO. (II) An aqueous solution of 0.02M zinc nitrate hexahydrate (Zn(NO3)2.6H2O, 99.998%) and 0.02M hexamethylenetetramine (HMT, (CH2) .6N4, 99+%) was stirred with a magnetic stir bar at 350 r.p.m for 10 minutes at room temperature yielding a clear solution. The solution pH before sonication was 7.21. (III) The Si substrate was then immersed into the aqueous solution and sonicated at 50% of the maximum amplitude of the 20kHz ultrasonic probe for 10 minutes providing the solution with an intensity of 21W.cm^{-2}. The solution was refreshed two more times (3 cycles total). Introducing a fresh solution has been shown to improve the aspect ratio.[9] The substrate was rinsed with DI water then dried with N2 after each cycle. (IV) The same experiment was conducted at 20% of the maximum amplitude to determine the effect of intensity providing 6W.cm^{-2}. Samples were imaged with FEI XL30-SFEG or Hitachi S-4500 field emission Scanning Electron Microscopes. All chemical reagents used in this report were used without further purification.

The growth described above was also conducted on Au coated Si and glass substrates as a proof of concept that this method can be implemented on diverse surfaces.

1.2 DISCUSSION AND ANALYSIS

As seen in figure 1, a rough seed-layer is deposited on an Au coated Si substrate via the method described above. This seed-layer was found to be necessary to ensure effective growth of the arrays. The deposition of a rough seed-layer is expected to increase the density of the ZnO NWs in the array while having a smooth seed-layer is expected to produce more oriented ZnO NWs.[10]

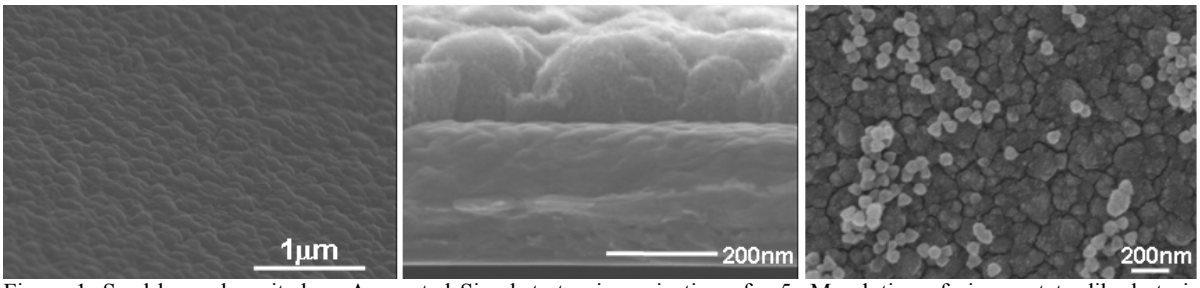

Figure 1. Seed-layer deposited on Au coated Si substrate via sonication of a 5mM solution of zinc acetate dihydrate in ethanol (shown in pan and cross-sectional views). A similar seed-layer can be deposited using the precursor in isopropanol (pan view).

Experiments by Jung et. al. have shown that sonication can aid the growth of ZnO nanowires.[5] ·OH, ·O2, ·HO2 and ·H radicals are produced in the sonication of water[5] and ·OH species can promote the growth of ZnO nanorods through the intermediate product of zinc hyroxide. The growth of ZnO NW arrays has been stated in the following manner[11-12]:

$$(CH_2)_6N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \quad [1]$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad [2]$$

$$Zn(NO_3)_6H_2O \rightarrow Zn^{2+} + 2NO_3^- \quad [3]$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad [4]$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad [5]$$

The photoluminescence (PL) spectrum of a ZnO seed-layer on gold is shown in figure 2. A dominant orange peak at about 580 nm is seen along with a minor ZnO peak observed at 363nm. A 325 nm HeCd laser was used to collect the spectrum.

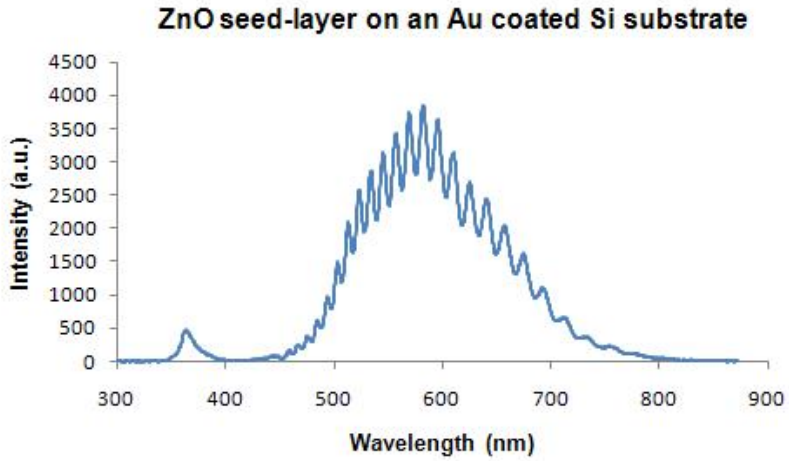

Figure 2. PL spectrum of ZnO thin-film seed-layer deposited via sonication. The oscillations in the orange peak result from the filter used to prevent the laser line from reaching the spectrometer.

This type of seed-layer was used to grow ZnO NWs under the specific conditions mentioned in the experimental section. The optimal growth conditions for oriented wires are 6W.cm2 intensity, 20% of the maximum amplitude, sonicated for 10 minutes each cycle. Three cycles were performed. Figure 3a shows the result. After this sample was placed on a hot-plate, hydrothermal, equimolar solution of HMT and zinc nitrate hexahydrate (0.02M) for two hours at 60^{o}C, we see that the wires get thinner but orientation stays relatively the same (figure 3b). The thin, dense wires shown in Figure 3b in comparison with figure 4 shows that with larger intensity, a similar wire obtained with hot-plate treatment is possible.

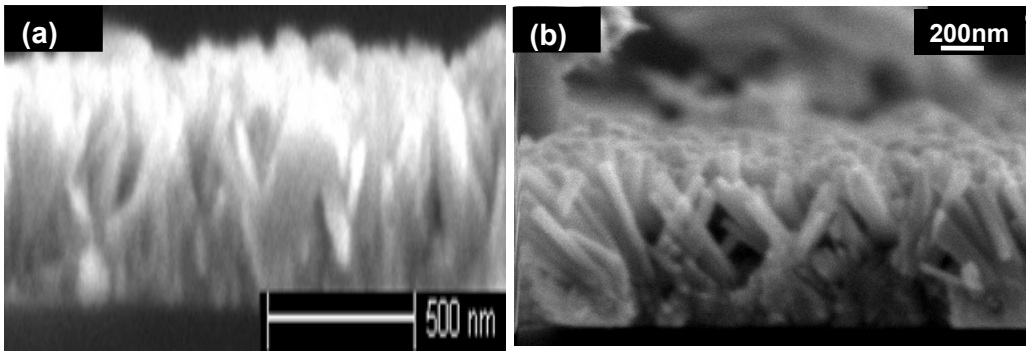

Figure 3. (a) SEM image of ZnO NWs grown with sonication at 19W.cm^2 (b) Hydrothermal treatment of (a) after 2 hours at 60^{o}C.

This shows that oriented wires can also be grown at higher intensities (21W.cm^{-2}) removing the need to introduce a hot-plate solution into the synthesis. At 50% of the maximum amplitude of the 20 kHz ultrasonic probe oriented ZnO NWs can be synthesized as seen in figure 4.

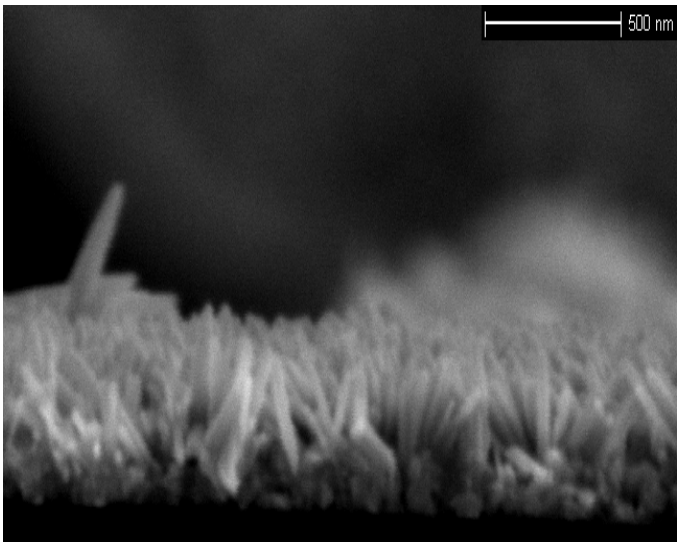

Figure 4. ZnO nanowires produced using an intensity of 21W·cm^{-2}.

The PL spectrum of a ZnO NW array under these conditions (21Wcm^{-2}) is shown in figure 5. This, in comparison to figure 2 shows a strong peak at the ZnO UV wavelength (377nm) along with the visible light defect peak[13]. This suggests that reasonable quality ZnO NWs were seeded by the low quality ZnO deposition under our mild growth process without the need for subsequent treatments such as annealing.

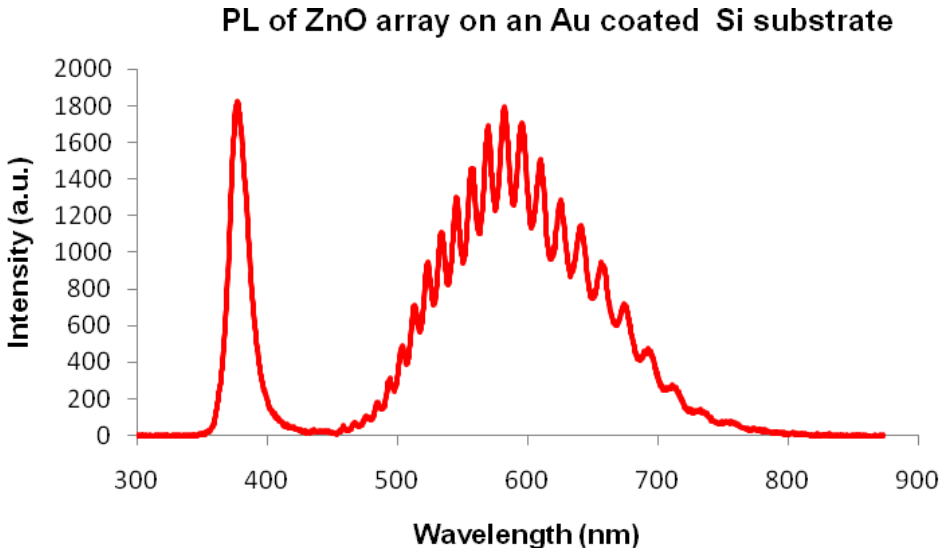

Figure 5. PL spectrum of a ZnO array produced via Sonication at 21 Wcm^{-2}.

Raman scattering was performed to assess the vibrational properties of the NWs. Both ZnO NW arrays investigated displayed a peak at 438 cm^{-1} which corresponds to the E_2^{High} nonpolar phonon mode, associated with oxygen.[14] The linewidth broadening of the peak to beyond a FWHM of 5 cm^{-1} has been attributed to isotopic inhomogeneity of the oxygen atoms in the material (i.e. the presence of 18O in addition to 16O).[15]

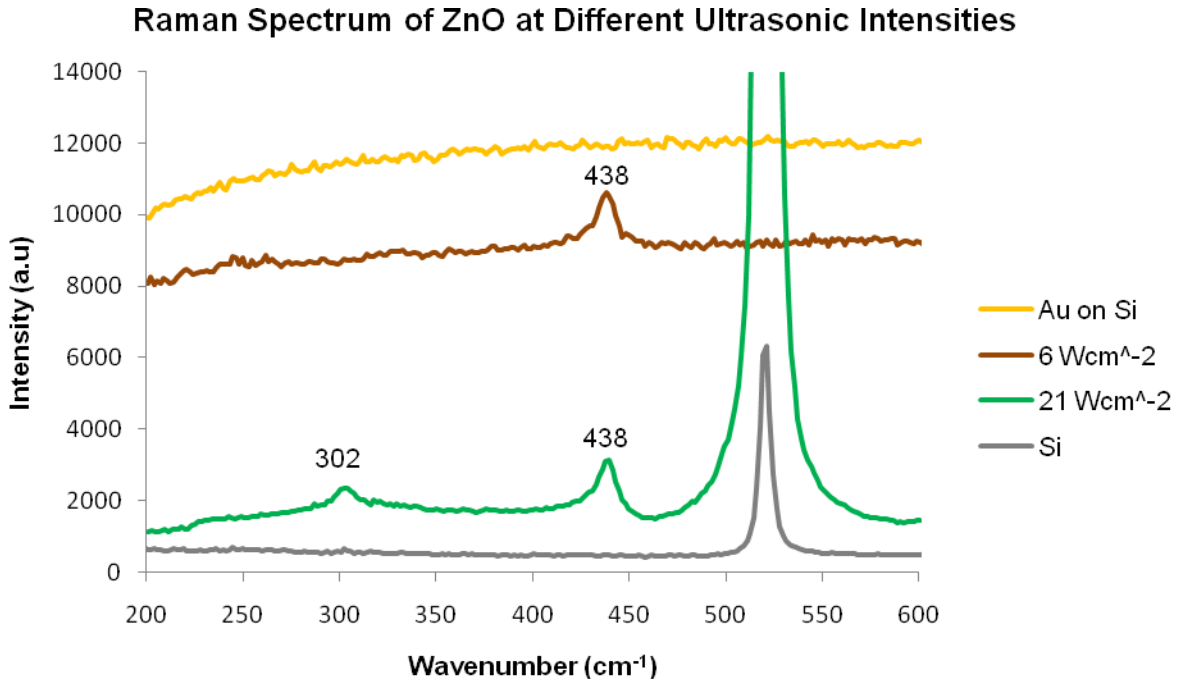

Figure 6. Raman scattering of ZnO samples prepared at different ultrasonic intensities.

The 302cm^{-1} peak seen wide in the 21 Wcm^{-2} sample is attributed to the Si substrate.[16]

To show that ZnO NW arrays can be grown on non-metallic and inexpensive surfaces, we deposited a ZnO seed-layer and then grew the ZnO nanowires on glass. Figure 7 shows the result of this growth.

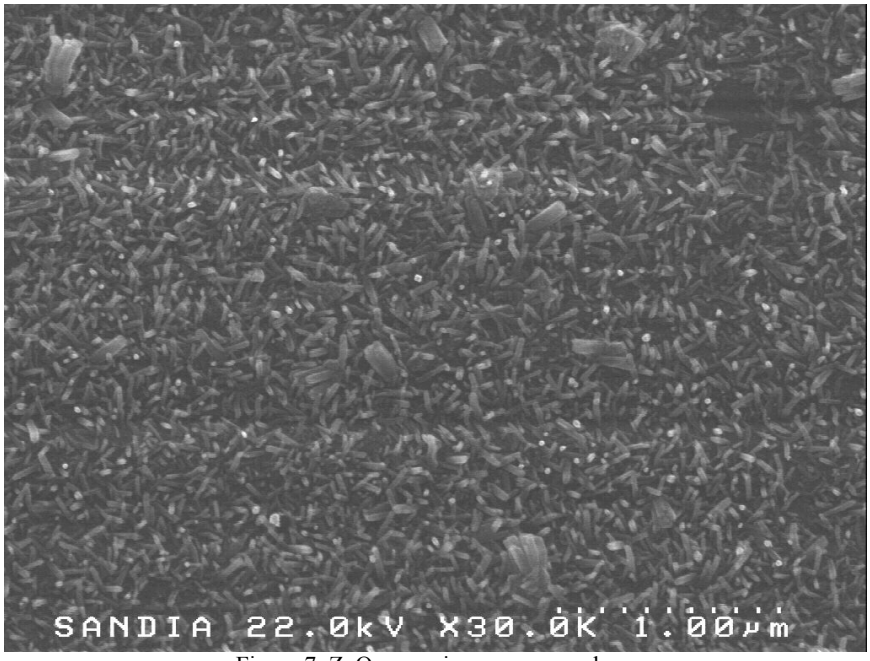

Figure 7. ZnO nanowires grown on glass.

Our average growth rate is ~600nmh^{-1}. Compared with other room-ambient approaches, our growth time is significantly smaller than other reported sonication syntheses[5].Compared to other literature, our growth rate is > 10 times that of conventional hydrothermal methods used which have a growth rate of 40nmh^{-1}. [17]

In this paper, we have presented an economical and rapid approach for growing ZnO NW arrays. Using just one system, we were able to deposit and grow the wires on conducting and insulating substrates of varied quality by sonochemical means. It is expected that this method will be useful in fabricating stand-alone and also integrated optoelectronic devices.

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