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Sonochemical Synthesis of Zinc Oxide Nanowire Arrays on Silicon and Glass Substrates

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Abstract:
Zinc Oxide (ZnO), a wide bandgap (3.37 eV) semiconductor with large exciton binding energy, has drawn considerable interest from a variety of disciplines including engineering, material science, and the biosciences. Several attractive optoelectronic properties such as excellent transparent conducting characteristics make it a good candidate for applications in solar cells, photodetectors, and displays. Its piezoelectric effect has also generated considerable interest for energy scavenging. For practical low cost nano-electronic applications, it is important to develop mass-manufacturable processes for fast and inexpensive ZnO nanowire production. Vertically aligned ZnO nanowires have been produced on relatively short timescales by sonication, but this method requires costly Zn substrates or the deposition of Zn thin films to serve as a seed layer. We report a purely sonochemical method for the seeding and synthesis of ZnO nanowire arrays that can be formed on virtually any substrate that is stable in alcohol and aqueous solutions. Vertically aligned ZnO nanowires were synthesized from a single solution at room-ambient with the help of ultrasonic excitation. Prior to the nanowire growth, a ZnO seed layer was deposited using the same system with an alcohol solution. The optimal conditions to produce a large density of oriented wires at room-ambient along with their electrical and optical characteristics are presented for ZnO nanowires with a significantly smaller growth time as compared with traditional growth techniques such as evaporation, chemical vapor deposition and sputtering. Our method promises a low cost, mass-manufacturable process for fast ZnO nanowire production for low cost electronic, optoelectronic and energy conversion applications on inexpensive substrates.

Keywords: Zinc Oxide Nanowires

1. Introduction:

Zinc Oxide (ZnO) materials have drawn considerable interest from a variety of disciplines including engineering, material science, and the biosciences. It is considered an important material for applications such as optical devices[1], solar cells[2], and energy harvesting[3]. Synthetic routes such as precipitation[4], pyrolysis[5] and hydrothermal[2, 6-7] methods have been used to synthesize ZnO nanomaterials. To mass manufacture ZnO nanowires on most substrates however, a simple, substrate independent, fast approach is needed. Sonochemical synthesis of vertical ZnO nanowires has been used before[8] but this method requires a costly Zn substrate or the deposition of a Zn thin-film prior to growth.

Here, we report a purely sonochemical method for seeding and synthesis of ZnO nanowire arrays on substrates that are stable in alcohol and aqueous solutions using just one system (750W ultrasonic processor, Sonics and Systems). The synthesis of ZnO nanowire arrays takes approximately 30 minutes excluding the 15 minutes required for seeding. Unlike the vapor-phase synthesis method, the hydrothermal method of growing ZnO NWs can be performed at substantially lower temperatures and self-evolving pressure. The reaction time for this synthesis of ZnO NWs however can take several hours, or even days[9]. In this report, we propose a method proceeding at room ambient pressure and temperature in less time, and using only one system. 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 technique was found to be advantageous from the viewpoint of environmental impact, scalability, process time, and production cost in comparison with other techniques [3, 10-11]. We also report on the transparency of each sonication cycle and seed-layer.

The growth process is explained schematically in figure 1. Substrates that can withstand alcohol and aqueous solution treatment can be used (Figure 1a). Figure 1b shows the deposition of a 200nm thin film of ZnO seed-layer. The time required for this deposition is 15minutes. Figure 1c shows the growth of ZnO nanowires vertically; the growth time is 10 minutes.

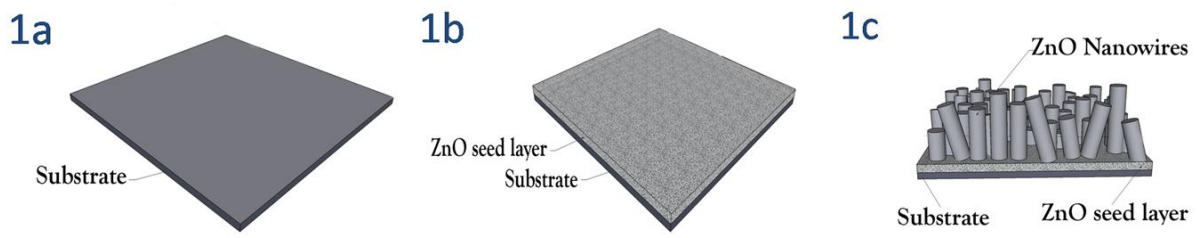

Figure 1. (a) Substrate that is stable in alcohol and aqueous solution (b) ZnO seed-layer deposition (c) ZnO nanowire growth

2. 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 ($C_4H_{10}O_6Zn$, 98$^+$%). The solution was sonicated for 15 minutes at an intensity of 21W·cm^{-2} (1.3cm horn diameter) at 20 kHz. The process was repeated once to deposit a continuous layer of ZnO. (II) An aqueous solution of 0.02M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.998%) and 0.02M hexamethylenetetramine (HMT, $(CH_2) \cdot 6N_4$, 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 in the aqueous solution and sonicated at 50% of the maximum amplitude of the 20 kHz ultrasonic probe for 10 minutes each cycle providing the solution with an intensity of 19W·cm^{-2}. The solution was refreshed two more times (3 cycles total). Introducing a fresh solution each time has been known to improve the aspect ratio.[12] The substrate was rinsed with DI water then dried with N_2 after each cycle.

The experiment described in (I-III) was also conducted on a glass substrate as a proof of concept that this method is applicable for inexpensive substrates.

All 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. Ocean Optics SpectraSuit was used to obtain optical transmission results.

3. Discussion and Analysis

As seen in Figure 2, a rough seed-layer is deposited on an Au coated Si substrate via sonication. This seed-layer needs to be deposited onto the substrate to ensure growth of ZnO NWs. The deposition of a rough seed-layer can increase the density of the ZnO NW array while having a smooth seed-layer can cause more oriented ZnO NWs.[13]

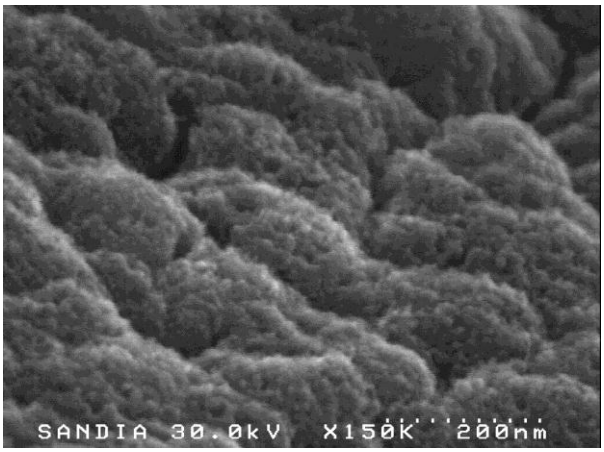

Figure 2. Seed-layer deposited on Au coated Si.

The peaks and valleys formed in the seed-layer deposition seen in Figure 2 can serve as nucleation spots and help in the formation of ZnO nanowires. Figure 3 shows the attempted growth of ZnO on a Si substrate without the deposition of the seed-layer. This control experiment shows poor ZnO coverage and the absence of NW arrays.

We find that ZnO NWs can be grown at 21W·cm^2 intensity, 50% of the maximum amplitude, with 10 minutes of sonication. Figure 4 shows the result.

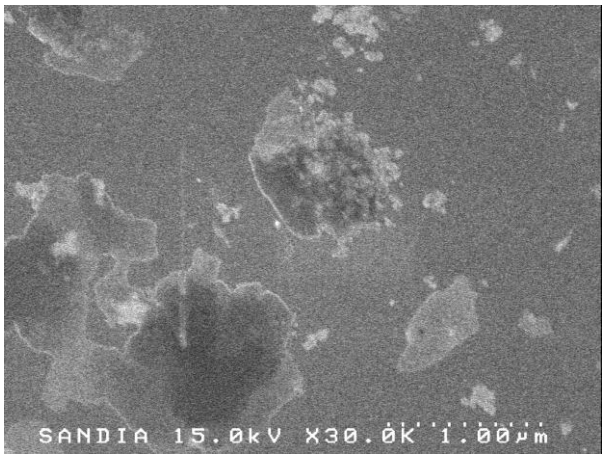

Figure 3. No nanowires are seen when no seed-layer is deposited.

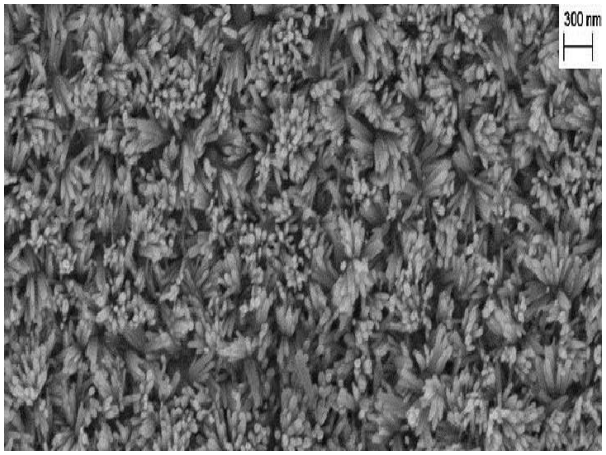

Figure 4. SEM image of ZnO NWs grown with sonication at 21W·cm^2

The cross-section SEM of the NWs shown in figure 4 is shown in Figure 5. This shows that at can be grown at 50% of the maximum amplitude of the 20 kHz ultrasonic probe (21W·cm^{-2}).

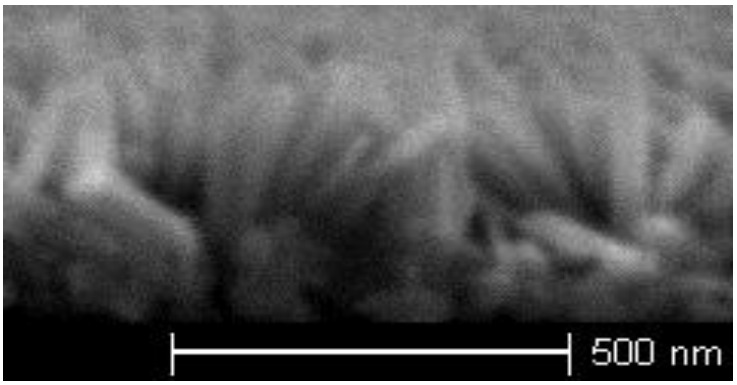

Figure 5. Cross-sectional image of ZnO nanowires produced using an intensity of 21W·cm^{-2}

As shown in Figure 6, the Raman peak at 438cm^{-1} indicates ZnO crystal structure and the 520cm^{-1} peak is attributed to the Si substrate.[14] The 438cm^{-1} corresponds to the E_2^{High} nonpolar phonon mode, associated with oxygen. [15]

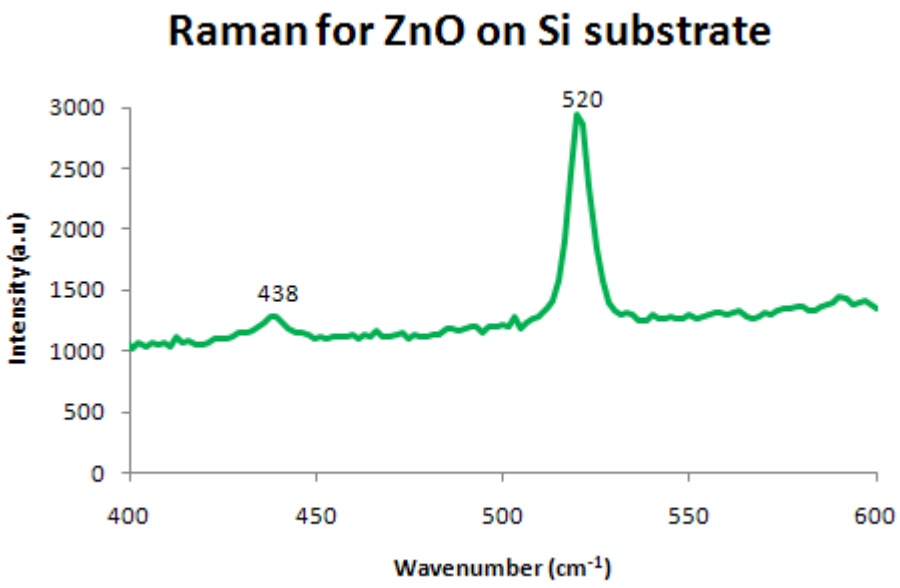

Figure 6. Raman spectra of ZnO on Si substrate.

To test for the transparency of the seeded ZnO and the ZnO nanowires, spectroscopy results are shown in Figure 7. The ZnO seed-layer and ZnO nanowire array was grown on glass. We find that the transmission characteristics do not change after the second coating of ZnO nanowires.

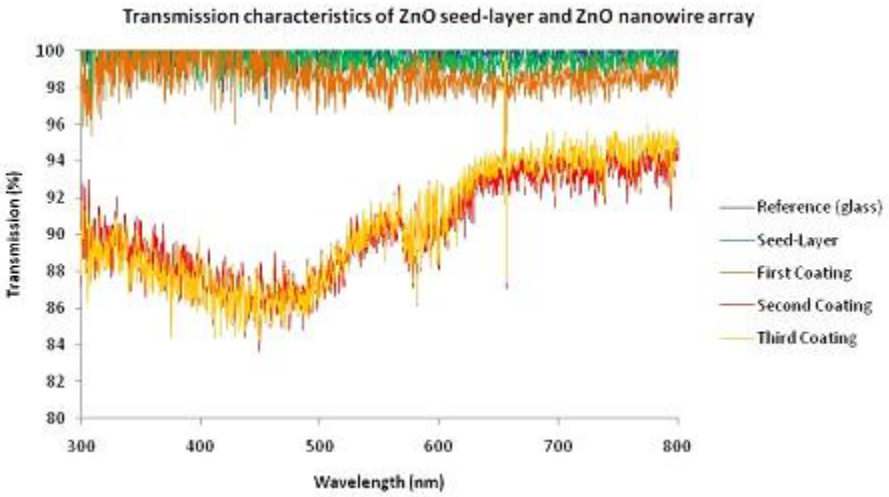

Figure 7. Transmission characteristics of ZnO seed-layer and ZnO nanowire array.

Our average growth rate is ~600nmh^{-1}. Compared with other room-ambient approaches, our growth time is significantly smaller than other reported sonication syntheses[8].Compared to other literature, our growth rate is > 10 times that of conventional hydrothermal methods used which have a growth rate of 40nmh^{-1}. [16]

Conclusion:

We demonstrated a purely sonochemical method for the seeding and synthesis of ZnO nanowire arrays which can withstand alcohol and aqueous solutions. Vertically aligned ZnO nanowires were synthesized from a single solution at room-ambient with the help of ultrasonic excitation. Prior to the nanowire growth, a ZnO seed layer was deposited using the sonicator system. The optimal conditions to produce a large density of oriented wires at room-ambient along with their electrical and optical characteristics are presented for ZnO nanowires with a significantly smaller growth time as compared with traditional growth techniques. Transmission characteristics show that we get ~92% transmission even after 3 cycles of treatment. We also find that transmission characteristics do not fluctuate drastically after multiple cycles. Our method promises a low cost, mass-manufacturable process for fast ZnO nanowire production for low cost electronic, optoelectronic and energy conversion applications on inexpensive substrates.

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