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Super-fast Synthesis of ZnO Nanowires by Microwave Air-Plasma

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Microwave radiation is focussed on the sharp edges of the Zn swarf. Plasma is produced by the microwave in the atmospheric condition and successfully used to synthesize ZnO nanowires and ZnO nanoparticles. The fabrication setup is very simple but extremely fast and effective. Microwave is irradiated to the sharp Zn swarf which is ignited and sputtered by the air plasma with a very high oxidization and crystallization rate.

Zinc oxide nanowires (ZnO Nanowires) are nanomaterials that have been extensively researched for last decade.[1-3] They are used in many applications such as a transistor, a gas sensor, photo catalysis, or an antibacterial chemical. [4-7] The fabrications of ZnO nanowires can be processed by many techniques for example sputtering,[8] vapor phase deposition,[9, 10]pulse laser deposition,[11] spray pyrolysis,[12] hydrothermal growth[13,14]. Though there are many available fabrication technologies, ZnO nanowire based devices or ZnO nanowire based products are yet to be widely commercialized in the modern market. Most of mentioned techniques are still lab-scale production.[15] Many of them require low pressure, an exact controlled temperature, and long vacuum and heating time. For example, vapor phase deposition requires a well mixing of ZnO and graphite powder, the furnace takes around 30 minutes to heat up and it takes more than 1 hour before the temperature of furnace is low enough to take the sample out. In order to reduce the production time and complexity, a rapid large scale mass production of ZnO nanowires has been proposed by Chunyu Ma et al, P. Singjai et al.[16, 17] The large scale ZnO nanowire fabrication techniques by Chunyu and Singjai were still using high temperature process to gradually evaporate Zn vapor from carbothermal reduction. The technique required a furnace, inert gas flowing, including expensive ZnO and graphite powders. To promote the larger scale applications, a lower cost and faster manufacturing process need to be invented. In this work, we propose a new method for an extremely rapid growth of ZnO nanowires.

A well investigated research about the ionized plasma from the microwave to grow ZnO nanowires had already been reported by Khaled A Elsayed and Alexander Irzh et al., however, the ultrahigh vacuum system and a very complicated setup were still mandatory to stabilize the plasma.[18,19] In the report from A Elsayed, the source for ZnO sputtering was an expensive and complex chemical, the production yield was as low as the other common techniques, and the production time was more than 30 minutes. Due to many complications in previous technologies, our method in this work combines the concept of metal-induced microwave ignition and plasma sputtering together which gives a much higher yield and much faster but simpler ZnO nanowire production. Usually when a piece of metal is in the microwave oven, it becomes a wave receptor which receives the incoming wave and reflects it back.[20]

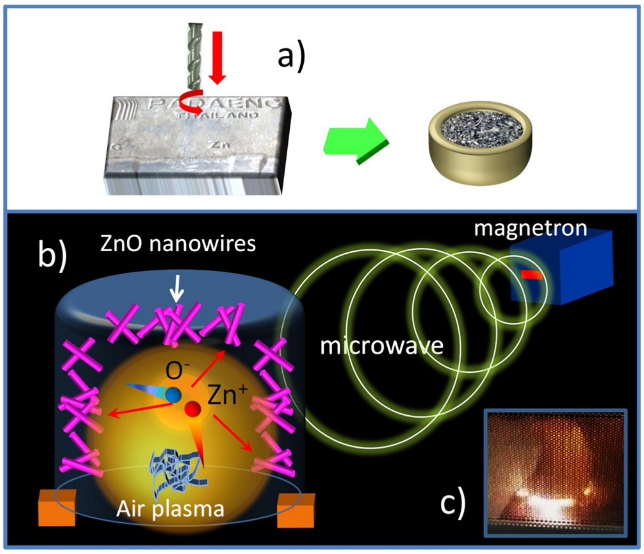

Figure 1. a) Zn ingot is drilled by a screw, Zn swarf is collected from drilling Zn ingot, and Zn swarf is placed in the middle of an alumina container, **b)** microwave is irradiated to the swarf and plasma spark, plasma sputters Zn atoms out and ZnO nanowires are deposited everywhere inside the chamber, **c)** the picture of air-plasma sputtering during the deposition process.

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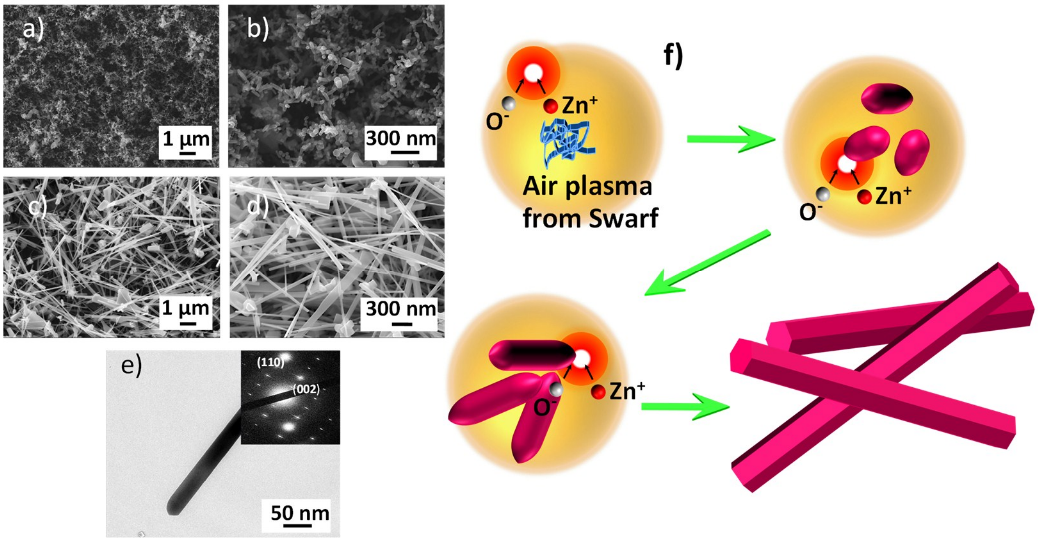

Figure 2. a) and **b)** SEM image of ZnO nanoparticles from the microwave air-plasma sputtering for 1 second, **c)** and **d)** SEM image of ZnO nanowires from the microwave air-plasma sputtering for 4 second. **e)** TEM image showing the ZnO nanowires of 60 nm diameter with the c-orientation growth. **f)** 4 steps for the ZnO nanowires formation by microwave air-plasma. The first step is the ionization and oxidation of Zn atom on the free space, the second step is the nuclei and nanoparticles formation during the plasma process, the third step is the elongation of nanoparticles to become the long ellipsoid ZnO nanoparticles, and the forth step is the completed ZnO nanowires after 4 second deposition.

The microwave induced an internal potential which generates a very high field at sharp peaks and edges of a metallic component such as aluminum foil.[21] At these sharp peaks, electrons can excite and the plasma arc occurs. Hence a sharp edge is needed in order to start the ignition from microwave. The same reason explains why plasma can be ignited by irradiating microwave to the sharp swarf. Swarf is the machining waste which was derived from drilling holes in Zn ingot as shown in Figure 1 a). During the microwave radiation, air plasma sputtered Zn atoms out of swarf. At the same time, Zn atoms oxidized and deposited on the whole area inside the container as shown in Figure 1 b). The synthesis area can be controlled by confining the plasma inside the alumina container in Figure 1 c). Because the major compositions of air are nitrogen and oxygen gases, the high energy plasma was expected to be ionized nitrogen atoms and ionized oxygen atoms which can sputter Zn atoms out of swarf. The Zn atoms oxidized and the ZnO nanowires grew with a preferential orientation (c-axis) which was shown in Figure 2 e). The products from the microwave air-plasma were Zn vapors, ZnO nanowires (deposition and floating fume), ozone, and nitrogen oxide. Nitrogen oxide and ozone were exhausted out of the hood, but deposited ZnO nanowires were collected inside the alumina container. When a glass substrate was placed at the sidewall of alumina chamber, ZnO nanowires were deposited on it. The deposition continued for 1 second and 4 seconds and the result was shown in Figure 2 a), b) and c), d) respectively. When deposition time is too short (1 second), ZnO nanoparticles was obtained everywhere on the substrate as shown in Figure 2 a) and b). The average particle size was 50 nm. The early state of ZnO nanoparticles were the incomplete ZnO nanowires which fully developed to the completed ZnO nanowires at a longer deposition time. One can observe that nanoparticles in Figure 2 a) and b) were not connected to each other. Therefore ZnO nanowires shown in Figure 1 c) and d) were grown freely from each other as well.

This result of nanoparticle formation implied that the early state of ZnO nanowire was not appearing in the shape of rods, but rather round and irregular long-ellipsoid nanoparticles.

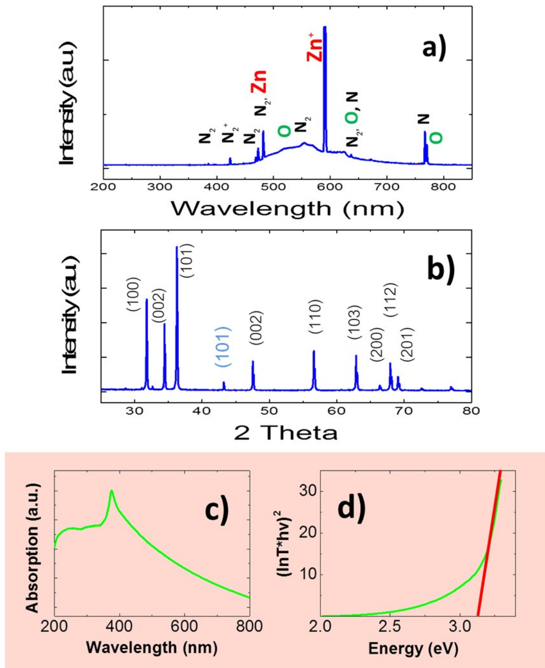

Figure 3. a) A plasma emission spectrum during microwave air-plasma process **b)** XRD of ZnO nanowires from microwave air-plasma process, **c)** UV-vis spectroscopy of ZnO nanowires, **d)** Tauc plot of showing the energy gap of ZnO nanowires.

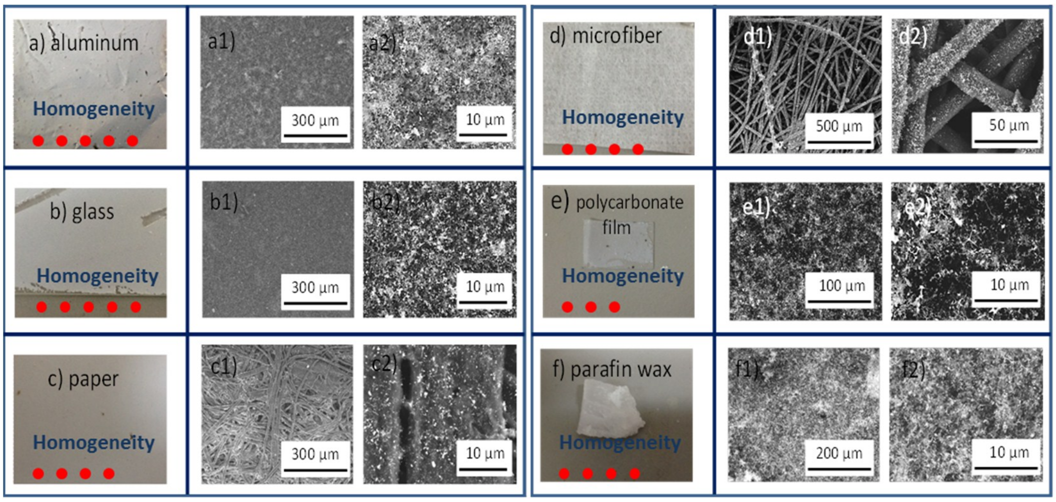

Figure 4. ZnO nanowires deposited on **a)** aluminum foil substrate, **b)** glass, **c)** paper, **d)** microfiber, **e)** polycarbonate film, **f)** paraffin wax. The red dots represent the degree of homogeneity of ZnO nanowires on each substrate.

ZnO nanowires had an average diameter of 65 nm. With a longer deposition time than 4 seconds, ZnO nanowires piled up on each other and the film become thicker. The growth of ZnO nanowires by this technique did not require catalysts on the substrate. Because both ZnO nanoparticles and ZnO nanowires were formed on the free space, they could not be grown vertically to the substrate and they were not rooted to the substrate. At this point, we can deduce the growth mechanism of ZnO nanowires into 4 steps as shown in Figure 2 f). At first, Zn atoms were sputtered out of swarf. They oxidized, deposited and agglomerated on the substrate without any catalysts. In the second step, a large amount of ZnO nuclei has generated and Zn atoms kept on oxidizing and developed into the bigger ZnO nanoparticles. For the third step, ZnO nanoparticles were prolonged and become irregular long ellipsoid particles. These long ellipsoid particles tended to organized itself to the most stable state which becomes ZnO nanowires in the fourth step.

The light from the plasma was extremely bright and the spectrum of plasma was inspected by Ocean optic spectrometer which was shown in Figure 3 a). The plasma emission spectrum composed of nitrogen, oxygen and Zn peaks which were a good proof that a large number of Zn atoms were sputtered out.[22-26] ZnO nanowires crystal orientation was observed by XRD as shown in Figure 3 b). The XRD pattern clearly confirmed the wurtzite structure of ZnO nanowires based on (JCPDS 65-3411) standard. However there was a small peak of metallic Zn at 43^{o} which implied a small fragment of incomplete oxidization of ZnO nanostructure.[27] This was common for ZnO nanowires grown by this technique because the process started and stopped very fast. Furthermore a small number of Zn atoms that gained high energy and swiftly impinge on the substrate cannot totally oxidize before many other Zn atoms deposited and buried them inside ZnO structure. Other than this small peak, the crystallographic property of ZnO nanowires grown by microwave air-plasma method is very impressive with only very short deposition time.

The optical property of ZnO nanowires was investigated by UV-vis absorption spectrometer. The result was shown in Figure 3 c). The absorption peak appeared at 376 nm did correspond to the UV range. The result of UV-vis absorption was the same as the result of UV-vis absorption in the other methods.[28,29] This is the confirmation that the optical property of ZnO nanorods from this method is not different from the others. The electronic band gap can be analyzed by Tauc plots in Figure 3 d) which was derived from Figure 3 c). The extrapolated value depicted the energy gap of 3.15 eV which was smaller than the real band gap. It implied that the near band edge excitonic absorption occurs and cause a lower absorption energy.[30] This phenomenon is very common in many wide band gap semiconductors especially in ZnO nanowires.

The microwave air-plasma technique can be used to grow ZnO nanowires on various substrates within 4 seconds at the same time. In Figure 4 a), ZnO nanowires can be grown on a flexible aluminum foil which had a thickness of 30 μm. Usually aluminum foil could be easily oxidized under a high temperature and the oxygen atmosphere. For the microwave air-plasma technique, the substrate temperature can be sufficiently low to prevent the oxidization of aluminum substrate. Figure 4 a1) and Figure 4 a2) shows a homogeneous distribution of ZnO nanowires on aluminum substrate microscopically. In Figure 4 b), ZnO nanowires were grown on an amorphous silica glass. Figure 4 b1 and b2 depicted that ZnO nanowires can distribute equally everywhere on the glass. Glass is one of most common substrate for growing ZnO nanowires and widely used in many applications.[31,32] In Figure 4 c), ZnO nanowires were grown on paper substrate. Growing ZnO nanowires on a paper is normally difficult for other techniques. Paper can be burn if exposed to a high temperature, and it can be disintegrated if immersed in water for a long time. However there were a few research groups which successfully grown ZnO nanowires on paper by hydrothermal technique but the paper had to be wet though.[33] In this work, ZnO nanowires homogeneously deposited on paper substrate without submerging to the water or exposed to high temperature as shown in Figure 4 c1 and c2). The deposition of ZnO nanowires on the paper is another development toward a paper-based electronic. The next substrate for growing ZnO nanowires in this work was spunbond polyester microfiber. Because the microfiber substrate composed of many layers of fibers on top of each other, ZnO nanowires could only deposit on the top most fiber layer as shown in Figure 4 d1 and d2). Unlike the hydrothermal and vapor phase deposition, the microwave air-plasma technique has a strong shadow deposition effect.[34] In Figure 4 e), polycarbonate sheet which has the melting point of 155 ^{o}C was used as a ZnO nanowire substrate. This transparent substrate was not a perfect substrate because ZnO nanowires did not distribute equally on the substrate as shown in Figure 4 e1 and e2. Although ZnO nanowires appeared equally by naked eyes, they microscopically agglomerated in some area and left some blank area without any deposition due to the electrostatic force on the substrate. Finally, an even lower melting point material can be used as a substrate in this work. ZnO nanowires were deposited on paraffin wax (60 ^{o}C melting point) as shown in Figure 4f), 4 f1), 4 f2). This is a good proof that this technique can use common used materials as substrates to deposit ZnO nanowires.

ZnO nanowires were grown by the microwave air-plasma technique. This technique allows a simple setup to synthesis ZnO nanowires with an extremely quick process. The average diameter of ZnO nanowires is 65 µm and the crystallographic quality of ZnO nanowires is still good. The energy gap of ZnO nanowires was approximately 3.15 eV which is narrower than the real band gap due to the excitons-related absorption. This technique has a very high deposition efficiency and suitable to deposit ZnO onto any substrates.

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