
Structural Analysis and Growth Mechanism of Zn/ZnO Nanowires in AAO Template by Electrodeposition

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Abstract: To fully understand the mechanism of forming Zn and ZnO nanowires in electrodeposition, Anodic Alumina Oxide (AAO) membrane was used to electrodeposit Zn/ZnO nanowires by varying the potential. The structure of electrodeposited Zn/ZnO nanowires is studied by means of X-ray diffraction and scanning electron microscopy. Different deposition parameters were used to obtain different structure of electrodeposited nanowires. At -1.4 V with pH2.5, the pure Zn nanowires are electrodeposited. By lowering the potential to -1.0 V with same electrolytic concentration and pH, the formed nanowires are mixture of Zn and ZnO. Further decrease in potential to -0.6V, electrodeposited nanowires are of pure ZnO. The size of the critical cluster decreases with increasing the over potential. The formation of pure ZnO nanowires can be attributed to the formation of large size critical Zn nuclei, the larger size of nuclei favors the formation of pure zinc oxides nanowires.

Keywords: Nanowires, AAO, Zn, ZnO, Nuclei

1. Introduction

ZnO is a multifunctional inorganic material, having probably the richest family of nanostructures among all materials, both in structures and properties [1]. It has a diverse group of growth morphologies, such as heterojunctions, nanocombs, nanoring's, Nano helices / Nano springs, nanobelts, nanowires, nanobows, nanocages etc [2]. Moreover, one-dimensional nanowires arrays [3], 3D network nanowires [4], and coaxial core-shell nanowires [5] have been synthesized. Zinc oxide crystallizes in three forms: hexagonal wurtzite, cubic zinblende, and cubic rocksalt (the rarely observed). The wurtzite structure is most stable at ambient conditions and thus most common [6]. The zinblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The rocksalt (NaCl-type) structure is only observed at relatively high pressures about

10 GPa [7]. Hexagonal and zinblende polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself). These morphologies are expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical and electromechanical nanodevices. Due to the most fascinating semiconductor nature, plenty of studies have been performed to probe the diverse properties of ZnO since 1950s' [8, 9]. Among the various semiconductor, zinc oxide has many amiable properties that include a direct and wide band gap (3.37eV), large excitation energy (60meV), a large piezoelectric constant, strong ultraviolet emissions, stable structure, high penetrability, and good conductivity [10].

Over the several years research, ZnO nanowires have been fabricated by various methods. Wu et al. fabricated ZnO nano

rods by chemical vapor deposition (CVD) [10]. Park *et al.* fabricated ZnO nano rods by metal organic vapor phase epitaxy (MOVPE). Huang *et al.* adopted the vapor-liquid-solid (VLS) method to fabricate ZnO nanowires [11]. Heo *et al.* employed catalyst driven molecular beam epitaxial fabrication of ZnO nano rods [12]. Grabowska *et al.* performed catalyst free fabrication by thermal evaporation [13]. Ramirez *et al.* [14]. Wang *et al.* [15] and Li *et al.* [16] fabricated ZnO nanowires by template assisted fabrication of one-dimensional (1-D) [17] and two dimensional (2-D) nanostructures [18] as well as in the design of various AAO based nanodevices. Template assisted fabrication of ZnO offers many remarkable advantages over other methods. For template assisted fabrication of ZnO nanowires, several techniques have been developed such as electrodeposition [19], sol-gel deposition [20] and chemical vapor deposition (CVD) [21, 22].

Igoriwallance and his coworkers [2000] synthesized hexagonally arranged nanowires of ZnO and accomplished from their experimental work that increased annealing temperature causes variation of crystallite size. Jin-guo wang demonstrate that the superconductivity displays a clear limit from bulk like to quasi-1D behavior, as treated by residual low-temperature resistance, when length of wire in term of diameter is reduced to 70nm (which is twenty times smaller than the bulk coherence length). Paret: *et al.*, [2009] have established that the mobility of electron of ZnO nanowires can reach to 1000 cm²/V is when at later it is coated with polyimide in order to decrease the electron trapping and scattering at surface. X. D. Bai: *et al.*, [2006] have settled an experimental method based on the electric-field-induced resonant excitation to measure the dissimilarity in mechanical properties of nanowires structures directly by using in situ. Haibo Zeng: *et al.*, [2009] improved the field emission performance to a considerable level by adjusting the Nanowires current density, uniformity, and tapering through selection of template size and deformation, and electrolyte composition. In line with the adjustments, the field-emission performance of the arrays is significantly improved [23]. Qiong Zhou and his co-workers clear from his experimental work that photocatalytic activities can be controlled by PH of electrolyte. It was shown that the photocatalytic activity of the nanowires was proportional to the length to diameter ratio of the nanowires, which was in turn controlled by the growth time and grain size of the seed layer. [24]

It can be conclude from the above literature that the morphology, lengths, diameter and growing directions of ZnO nanostructures could be controlled by adjusting the parameters in the manufacturing process. The ability to control the synthesis of high quality ZnO nanowires leads to potential applications in UV photodetection, gas sensing, light-emitting nanodevices and transparent electronics. Among the number of Nanodevices which are composed using One-dimensional ZnO nanostructures such as nano-lasers, nano-detectors, and nano-sensors have fundamental potential applications [25]. Therefore the controlled and large scale synthesis of these one dimensional nanomaterials are of

potential importance [18].

2. Material and Methods

Synthesis by Electrochemical deposition in a template has been a multipurpose and specifically simple method, especially during the formation of metal nanowires. Nanowires array are obtained by filling pores of template which consist on a large number of vertically aligned cylindrical holes along with a distribution of narrow size. The structures of the nanowires fabricated by explained technique can also be controlled by regulating the deposition conditions, for instance pH value, deposition potential, additives and temperature.

The electrolyte was 0.1M ZnCl₂ and 0.65M H₃BO₃ aqueous solution with pH 3 adjusted by 1M H₂SO₄. Prior to electrodeposition, Au (gold) film was sputtered on the back side of membrane to assist as the conducting cathode lead. Pure graphite was used as an anode lead and saturated calomel electrode (SCE) as reference electrode. Deposition were performed at three different potentials (-0.6V, -1.0V, and -1.4V). All experiments were carried out at room temperature (25°C). X-ray diffraction (XRD, X'Pert PRO MRD, PANalytical, Netherland) with Cu-K_α radiation, and scanning Electron Microscopy (SEM, JEOL JSM-6700F) were used for the structural and morphological analysis, respectively. To perform the SEM observations, the AAO template is partly dissolve with a 5 wt% NaOH solution, then the rinsed with deionized water for several times.

3. Results

Figure 1 shows the XRD pattern for Zn/ZnO nanowires deposited at room temperature with pH 3 in the bath containing 0.1M electrolytic concentration at potential -1.4 V. Three peaks (100), (101) and (102) for Zn nanowires were observed at $2\theta = 39.01$ ($d=2.309\text{\AA}$), 43.23 ($d=2.091\text{\AA}$), and 54.37 ($d=1.687\text{\AA}$) degrees, respectively (File No. 65-3358). Whereas, other five peaks (111), (200), (220), (311) and (222) are for ZnO nanowires and are in agreement with the standard peak diffraction pattern (File No. 65-682). The values of 2θ degrees and interplanar spacing (d) are given in the table 1. At -1.0V, the peak intensity decreases for (100), and (101), and at $2\theta = 54.37$ ($d=1.687\text{\AA}$) degrees vanishes as can be seen in Figure 2. By lowering the potential to -0.6V (Figure 3), all the peaks appeared for pure ZnO nanowires, there is no XRD peak for Zn nanowires. From the XRD results, it is obvious that the growth of Zn/ZnO nanowires lies on the deposition potentials. At higher voltage (-1.4V) there was mixture of Zn and ZnO nanowires, by lowering the deposition potential value to (-0.6V) vanishes the XRD structural peaks for Zn nanowires and pure ZnO nanowires are obtained. The reason for the growth of pure ZnO nanowires in cylindrical pore of AAO templates is discussed in next section.

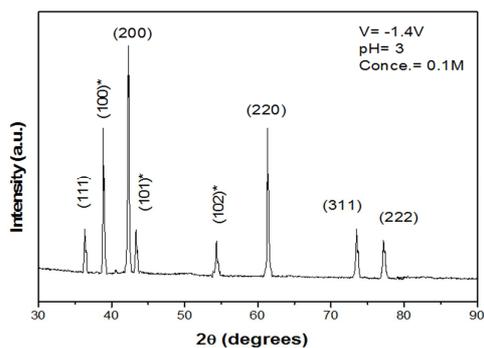


Figure 1. XRD patterns of Zn/ZnO nanowires deposited into the nanopores of AAO templates at room temperature (25°C) with deposition potential of -1.4V.

Table 1. Analysis of X-ray diffraction patterns for Zn nanowires, with reference to standard diffraction data (File No 65-3358).

Planes	Interplanar spacing (d)	Angle (2θ)
(100)	2.3079	39.01
(101)	2.0915	43.23
(102)	1.6874	54.37

Table 2. Analysis of X-ray diffraction patterns for ZnO nanowires in agreement with the standard diffraction data (File No 65-682).

Plane	Interplanar spacing (d)	Angle (2θ)
(111)	2.465	36.43
(200)	2.135	42.40
(220)	1.509	61.39
(311)	1.287	73.56
(222)	1.2326	77.38

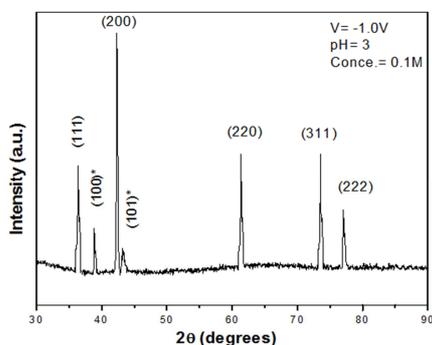


Figure 2. XRD patterns of Zn/ZnO electrodeposited in AAO templates at -1.0V.

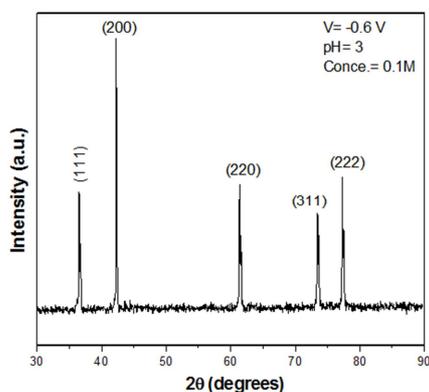


Figure 3. XRD patterns of pure ZnO nanowires electrodeposited in AAO templates at -0.6V.

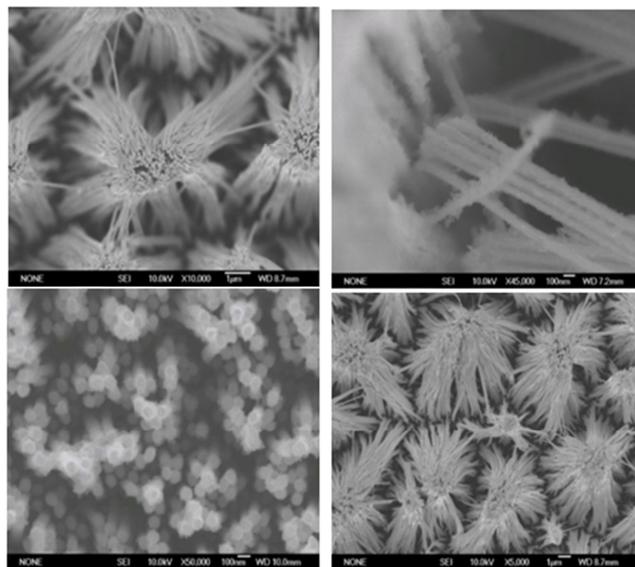


Figure 4. Top view of Zn/ZnO nanowires: SEM images of deposited nanowires at room temperature with pH 3 a) at -0.6 V b) at -1.0 V c) -1.4 V and d) larger view of ZnO nanowires at -0.6 V.

Figure 4 shows a typical top view SEM image of Zn/ZnO nanowires deposited at -0.6 V b) at -1.0 V c) -1.4 V and d) larger view of ZnO nanowires at -0.6 V. The diameter of the Zn/ZnO nanowires (~50 nm) is the same as that of the nanopores of AAO template, indicating that the nanopores of the AAO template were fully filled with Zn/ZnO atoms during electrodeposition.

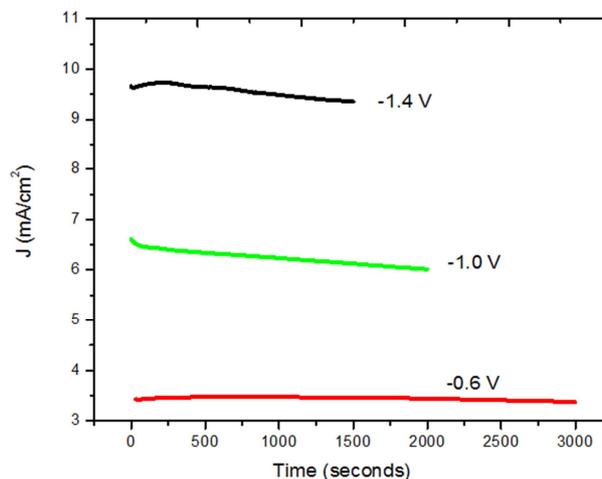


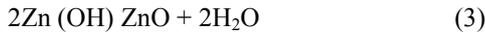
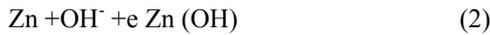
Figure 5. Current density vs time graph for the electrodepositing Zn/ZnO nanowires at various potentials.

Figure 5 current density vs time graph for depositing Zn/ZnO nanowires in AAO template at -0.6 V, -1.0 V and -1.4 V at room temperature. At potentials (-0.6V, -1.0 V, and -1.4V) the value of average current densities are approximately 3.4mA/cm², 6.5 mA/cm² and 9.6 mA/cm², respectively. The time to fully fill the nanopores of AAO templates varies with respect to the potential. At higher voltage (-1.4V), the recorded time is about 1500s. At deposition potential of -1.0V and -0.6V, the time for the growth of Zn/ZnO nanowires increases approximately to

2100s and 3000s, respectively. This current density v/s time curve shows that the growth rate for the Zn/ZnO depends on the deposition potential. By increasing the potential the growth rate of Zn/ZnO nanowires decreases.

4. Discussion

In electrodeposition of metal, metal ion M^{n+} is transferred into the ionic metal lattice $M_{solution}^{z+} + ze \rightarrow M_{lattice}$ from solution, in the meantime electrons are obtained from the external electron source to the metal M [41]. The metal ion becomes a neutral metal atom when an adsorbed hydrated metal ion catches the electrons from the surface by quantum-mechanical tunneling. An electrostatic interaction between the water molecules and neutral metal atom is zero and the water molecules are displaced. The neutral metal atom which is absorbed on the surface and also diffuses to a surface site where it will incorporate with the ionic metal lattice, which leads toward the growth of nanowires. The current density rises from valence electrons tunneling to hydrated metal and hydrogen ions, resulting metal nanowires growth and hydrogen evolution, respectively.



According to the free electron gas model, the metal are to be considered as potential box, which is filled with electrons to the Fermi level, that is lying below the vacuum level with the numerous electron volts. The distance from Fermi to vacuum level is known as the work function, as shown in the Figure 6.

$$E = V/d \quad (4)$$

Whereas the V is an applied potential to metal, and we suppose the potential of solution is (0) zero while d is the double layer width. ϵ is the potential energy of electrons outside of the metal which will change by changing the field. Most part of the electron tunneling occurs in the vicinity of the Fermi level which will have thinnest barrier.

It is renowned that by increasing the applied potential current density also increases. To clarify this statement we have use electron tunneling theory. From equation (4), it is observed that the electric field strength will become stronger. This gives idea for rapid change of potential of the electrons outside of the metal, shown in Figure 6. In this case, we get steeper slope of electronic potential with a higher electric field as compared to the small electric field. Width of barrier where electrons tunnel gets thinner and then tunneling process becomes easier. Hence, the current density value for Zn/ZnO nanowires at higher potential (-1.4V) is 9.6 mA/cm² which is greater than 3.4mA/cm² at low potential (-0.6V). Therefore, by increasing the applied potential the current density increases for the depositing nanowires.

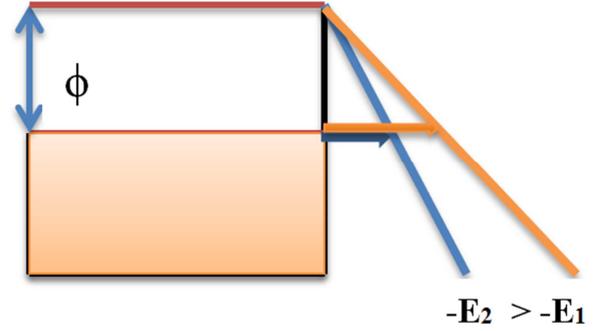


Figure 6. Schematic representation of transmission of electrons near the vicinity of Fermi level (E_F) through the potential barrier: effect of applied field (or electric field strength) on the barrier width (d) of electron tunneling.

For formation of metal nanowires in electrodeposition process, the metal ions which are hydrated in the solution reach at the surface of metal and are neutralized with the help of electron tunneling, and at the surface there would be formation of ad-atoms [42]. These ad-atoms can be move from a cluster of ad atoms. Rendering to the Classic electrochemical nucleation theory, the free energy of formation of a 3dimension cluster of N atoms, $\Delta G (N)$ is,

$$\Delta G (N) = -Nze\eta + bN^{2/3} \quad (5)$$

z is the hydrated metal ions valancy, e is an electric charge, η is an over potential and b is the constant which depends on the cluster geometrical shape. Deriving the Eq. (5) with respect to N and equating to zero yields the size of the critical cluster (N_c)

$$N_c = (2b/3ze\eta)^3 \quad (6)$$

It is observed that size of the critical cluster N_c almost relays on both over potential ($\eta = V - V_{eq}$, V is the applied

potential, and $V_{eq} = V_0 + \frac{RT}{zF} \ln[a]$) and on the shape of the

cluster. By increasing the over potential, size of critical cluster decreases. Formation of Zn atoms arises on a Au surface. The structure of the polycrystalline Au is rough and have irregular geometrical shapes in nanoscale. This leads to the clusters which are formed on the surface of polycrystalline Au and have various shapes and it can then be observe from Equation (6) that by the fixed deposition potential the sizes of N_c would have a distribution because of different shape factors. Furthermore, sizes of all critical clusters at the low potential of -0.6V are large, which are determined by Equation. (6). It will favor the formation of large sized nuclei of Zn which further interacts with the OH⁻ ions present in the nanopores for the formation of ZnO nanowires. The distribution of N_c size shifts toward the smaller one when the potential value is increases to -1.0 V, in which a small fractions of N_c are small enough that they can form crystal nuclei of pure Zn. Hence, coexistence of Zn-ZnO nanowires is observed. Thus, small fractions of the Zn crystals formed in nanowires, as can be seen in Figure 2. At -1.4 V, the fractions of the Zn nuclei are increases moderately as the distribution of size of N_c shifts to small size. At -1.4 V,

mostly the critical clusters size are present in the array of forming nuclei of Zn and hence fraction of Zn nanowires increases as observed. We can conclude from this discussion that critical nucleus of larger size favors the formation of ZnO nanowires.

Figure 7 further approves the growth of ZnO nanowires which is related to the size of critical nucleus and therefore on the applied potential. Figure 1.7a, displays that at high potential (-1.4V), the size of N_c is small and thus the interaction of these critical clusters with OH^- is less, so the fractions of Zn nanowires are large at high potential as can be seen in Figure 7. When the potential is low (-1.0V) the sizes of critical cluster become large, these large clusters can react with the OH^- ions which are present in porous template will form ZnO nanowires. Therefore, fractions of Zn nanowires decreases with the increase in potential. At lower potential (-0.6V), size of the N_c is large enough to do the interaction with the hydroxyl ions in the nanopores to form pure ZnO nanowires as can be confirmed by Figure 7.

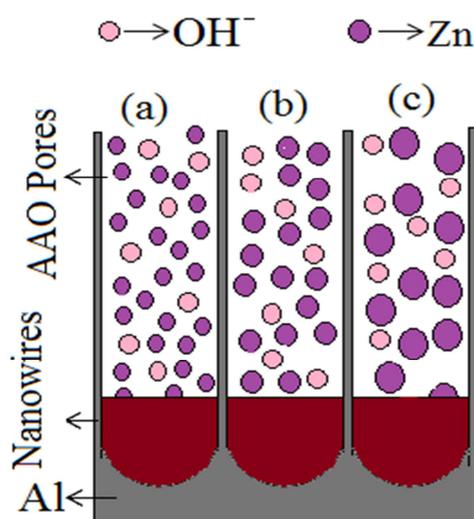


Figure 7. Schematic illustration showing the formation of ZnO nanowires in pores of AAO template: (a) high voltage (-1.4V) forming small Zn⁺ nuclei, (b) Less high voltage (-1.0) and (c) low voltage (-0.6) forming large Zn⁺ nuclei.

5. Conclusions

It can be concluded that at low potential favors the formation of pure ZnO nanowires, while at higher potential there would be mixture of Zn and ZnO nanowires. It means that the formation of pure ZnO nanowires can be attributed to the formation of large size critical Zn nuclei, the larger size of nuclei favors the formation of pure zinc oxides nanowires.

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