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Rapid Communication

Sixfold self-assembled hierarchical structures synthesized by direct annealing of Zn microtips

C.Y. Kuan[a], J.M. Chou[b], I.C. Leu[c,*], M.H. Hon[a]

[a]Department of Materials Science and Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC
[b]Department of Materials Science and Engineering, I-Shou University, Kaohsiung Hsien 840, Taiwan, ROC
[c]Department of Materials Science and Engineering, National United University, Miao-Li 360, Taiwan, ROC

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Abstract

A facile route and the related mechanism for forming sixfold core–shell hierarchical structure with well-defined anisotropic three-dimensional arrays have been described. The regularity and symmetry of hierarchical structures prepared by annealing Zn microtips are superior to the random nanostructure arrays formed in general vapor system reported in the literature. Owing to the distinct stress distribution on the topography of microtips during annealing, the mechanism for growing branched zinc oxide (ZnO) nanowhiskers is related to the relaxation of stress. In addition, the self-assembled hierarchical structures with naturally good contact results in a lowered energy barrier between Zn metal and ZnO semiconductor, which in turn gives a much better emission property.

Keywords: Annealing; Hierarchical; ZnO; Field emission

1. Introduction

In recent years, zinc oxide (ZnO) has attracted great interest because of its unique properties and multifunctional applications, such as, sensor, field electron emitters, light emitters, and electronic devices. However, the diversities of hierarchical nanoarchitectures of materials that possess not only high surface area but also structural integrity may provide some advanced applications. Therefore, controlling and exploring novel nanoarchitectures are important in understanding the crystal growth mechanism and to further develop new functional devices. Novel three-dimensional (3D) hierarchical nanoarchitectures of materials may find applications in a variety of fields that require not only high surface area but also structural integrity. So far, the synthetic approaches for nanoarchitectures can be generally classified into two categories: vapor-phase growth [1] and solution-phase growth [2]. However, the control of the regularity for 3D hierarchical structure is a challenging task, and the regularity is now commonly controlled by metal catalyst through the vapor–liquid–solid mechanism [3]. The solution-based process has also been developed for the formation of 3D hierarchical structures, but organic structure-directing agents are commonly chosen as templates [4].

In comparison to complex thermal evaporation technique, thermal oxidation of metallic foil provides a simple, convenient, and fast method for synthesizing nanostructures [5]. In addition, it is not easy to obtain the 3D hierarchical structures by thermal oxidation method, and the regularity of nanoarchitectures thus obtained is not desirable. Herein, direct thermal oxidation method without any catalyst is adopted, and novel 3D hierarchical structures are successfully obtained. A new and more controllable hierarchical morphology is demonstrated, and provides a new rationale pertaining to the design of new types of ordered nanostructures. Besides, the method can be extended to other similar metallic materials for specific applications.

*Corresponding author. Present address: 1, Lien-Da Rd., Kung Ching Li, Miao-Li 360 Taiwan, ROC. Fax: +886 6 2380208.
E-mail address: icleu@mail.mse.ncku.edu.tw (I.C. Leu).

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2. Experimental procedure

A polycrystalline Zn foil (99.9%, Alfa Aesar) was mechanically polished, followed by electropolishing with 2:1 volume mixture of 99.8% ethanol and 85% phosphoric acid at a current density of $69\,\mathrm{mA/cm^2}$ for 10 min. The single-crystalline Zn pyramid microstructures were prepared by anodic etching on electrolpolished polycrystalline Zn foil, which was conducted in NH_4Cl/H_2O_2 (molar ratio $NH_4Cl/H_2O_2 = 32$) solution using a constant current density $55\,\mathrm{mA/cm^2}$ for 60 s [6]. Then, the single-crystalline Zn pyramids were kept at 375 °C for 12 h in air. The hierarchical structures thus obtained were characterized by a field-emission scanning electron microscope (FE-SEM, XL-40FEG, Philips), and the structural properties are studied by transmission electron microscopy (FEG-TEM, Tecnai F20 G2 MAT, FEI). The field-emission characteristics of the hierarchical structures were determined in a chamber with a base vacuum of 5×10^{-6} Torr, and a Keithley 237 was employed as a power supply and a current meter.

3. Results and discussion

The single-crystalline Zn microtips are employed as substrates for branched ZnO nanowhisker growth, as shown in Fig. 1. Metallic Zn microtip arrays are shown in Fig. 1(a), in which the facets on Zn microtips are apparent. The selected area diffraction pattern (SADP) as inset of Fig. 1(a) exhibits its single-crystalline nature and the $\{01\bar{1}0\}$ spots from facets. Detailed analysis of the formation of single-crystalline Zn microtips has been reported [6]. Zinc is a volatile element and inclines to react with oxygen and forms oxide when exposed to oxygen or air. The 3D hierarchical structures are obtained under annealing treatment at 375 °C for 12 h as shown in Fig. 1(b). The self-assembled hierarchical structures consist of Zn microtips and ZnO nanostructures. However, the branched ZnO nanowhiskers exhibit preferred orientations, suggesting that the branched nanostructures might have a preferred growth direction, and maintain a well-defined relationship to the Zn stem. A detailed analysis will be given in later paragraph. Furthermore, an enlarged section as shown in Fig. 1(c) at the branched ZnO nanowhiskers indicates that the diameter and length are not uniform. Even though, an interpretation about the influence of temperature during annealing on nanostructure characteristics, such as, diameter and length has been reported elsewhere [7]. The influence of annealing temperature is both on the number density and the aspect ratio; however, some further work is now under way to further study the effect of the parameters on growth characteristics of ZnO branches.

So far, the synthesis of metallic oxide hierarchical structures by direct annealing has been reported only for CuZn alloy (brass) foil [8] and metallic particle [9]. However, the arrays of the self-assembled structures reported are not uniform, and it is randomly deposited on substrates. In general, for application to functional devices, it is necessary to prepare hierarchical structures as regular arrays. While the regularity of one-dimensional (1D) nanostructure arrays acquired from usual annealing procedure is not uniform. Therefore, it is important for the improvement not only for regularity but also for the integral symmetry. Herein, the self-assembled hierarchical structures on Zn microtips prepared from foils differ from

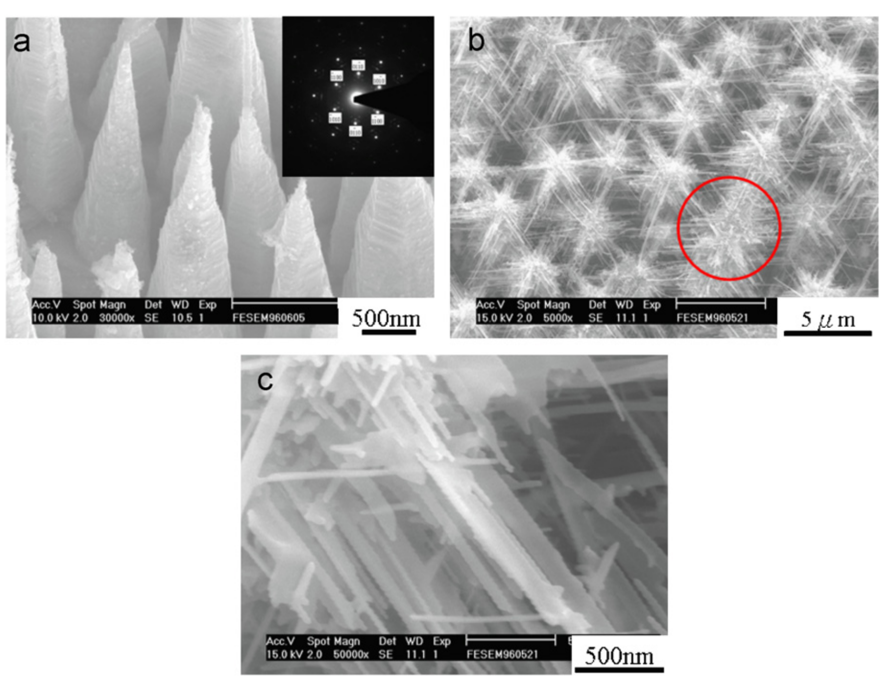

Fig. 1. (a) Arrays of Zn microtips after anisotropic anodic etching, (b) hierarchical structures after anneal at 375 °C, and (c) an enlarged image from (b).

the other similar 1D nanostructures, in that the whole 3D arrays is uniform and is guided by the substrate pattern. The procedure for forming 3D arrays on Zn foil provides a simple concept for morphology control and device integration. In brief, a facile method for forming hierarchical, symmetrical, and core–shelled structures has been demonstrated. Besides, through further adjustment of synthesis parameters including, annealing temperature, annealing time, and patterning, etc., more perfectly and orderly self-assembled 3D structures can be prepared.

Several mechanisms for nanostructure formation under vapor-phase system are proposed, including vapor–liquid–solid (VLS)/vapor–solid (VS) mechanism [10,11], self-catalyst mechanism [12], and relaxation of stress [7] and so on. There is no noble metal or nanosized transition metal observed at the tip of the branching ZnO nanowhiskers, i.e., the growth mechanism for the present branching is not related to the VLS models. Whether VLS or VS mechanism, a temperature above melting point is required for liquefying metallic particle regarded as catalyst. The operating temperature above melting temperature is also demanded for self-catalyst mechanism [12]. Therefore, the formation of ZnO nanowhiskers in this study, contrasting with the self-catalyst growth, and can not be attributed to the self-catalyst model. For low-melting point metals, the atoms are easy to diffuse, hence the whiskers may often be formed by spontaneous growth. In the past, the formation mechanism of conventional tin whiskers at room temperature has been reported; however, it is caused by the biaxial compressive stress between different grain orientations on polycrystalline substrates [13]. However, the tin whisker growth at room temperature does not correspond to the point of thermodynamics but kinetics, i.e. is expansion of dislocation loops by climb. Therefore, the formation of metallic whiskers is via a path of atomic transportation by surface migration.

Consequently, the possible mechanism for branched ZnO nanowhiskers is the relaxation of stress. The schematic diagram of the formation mechanism for hierarchical structures under annealing process can be illustrated (shown in Fig. 2). Firstly, even when the operating temperature is below the melting temperature of Zn foil (419.5 °C), a dense oxide film is formed on zinc microtips [14] as shown in Fig. 2(b). The presence of the dense ZnO film formed on the surface has been evidenced by TEM analysis prepared by focused ion beam micromachining (not shown here), and the thickness of shelled ZnO is about 107 nm. Owing to the phenomenon that the condensed oxide film shields the internal metal from the air, the oxidation rate will be reduced with time. In addition, the stress distribution during annealing is related to the topography of surface, and the influence of topography on stress concentration has been demonstrated [15]. The authors claimed that the cusp-like surface is the region with the highest degree of stress concentration. The conclusion suggests that the corner of the microtips is the energetically favorable site for the growth of nanowhiskers. Therefore, the corner of sixfold Zn microtips is the favorable sites for stress concentration as shown in Fig. 2(c). As long as the oxidation process continues through the diffusion of oxygen, stress is accumulated and after reaching a critical limit the oxide layer relaxes itself by spontaneous growth of nanowires from the surface [7]. The development of microstructure is from the corner and leads to the formation and growth of the branched nanostructures (shown in Fig. 2(d)). In addition, the branching ZnO growth phenomenon is also observed on rib pattern as shown in Fig. 1(b); in other words, the ZnO branches grow from the localized protruded sites. The result further confirms that the main factor for branch growth is related to cusp-like surface, i.e., is corresponding to the distribution of stress. Consequently, the mechanism for branched growth under thermal annealing is stress relaxation, and results in forming the novel hierarchical structure.

The individual structure of the branching ZnO nanowhiskers acquired under 375 °C annealing for 12 h is examined by TEM. A typical TEM morphology of a single ZnO nanostructure is shown in Fig. 3(a), which is straight with a diameter of 35 nm. The corresponding selected area electron diffraction (SAED) pattern confirms the single-crystalline structure as shown in Fig. 3(b), and the indexing of the SAED pattern is along the [0001] axis. The result of ED pattern in Fig. 3(b) indicates that the growth direction is along $\langle 11\bar{2}0\rangle$. It is also clearly shown that there is no obvious crystalline defect in the ZnO nanowhiskers, suggesting a relatively high quality of crystallization, and indicating that the facet of ZnO nanowhiskers is $\{01\bar{1}0\}$. Furthermore, a high-resolution TEM image is displayed in Fig. 3(c), and the result of lattice spacing 0.28 nm is in a good agreement with that for

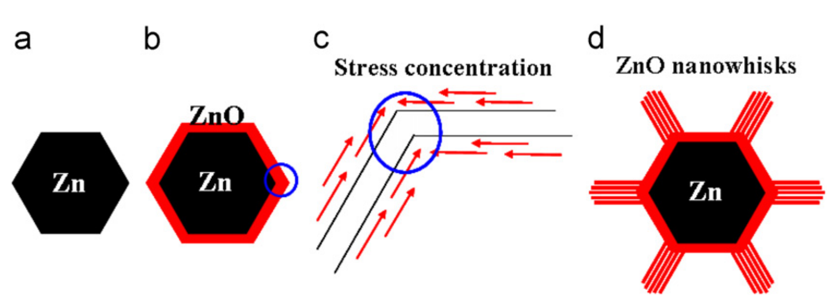

Fig. 2. Schematic diagram showing the formation mechanism of branched ZnO nanowhiskers.

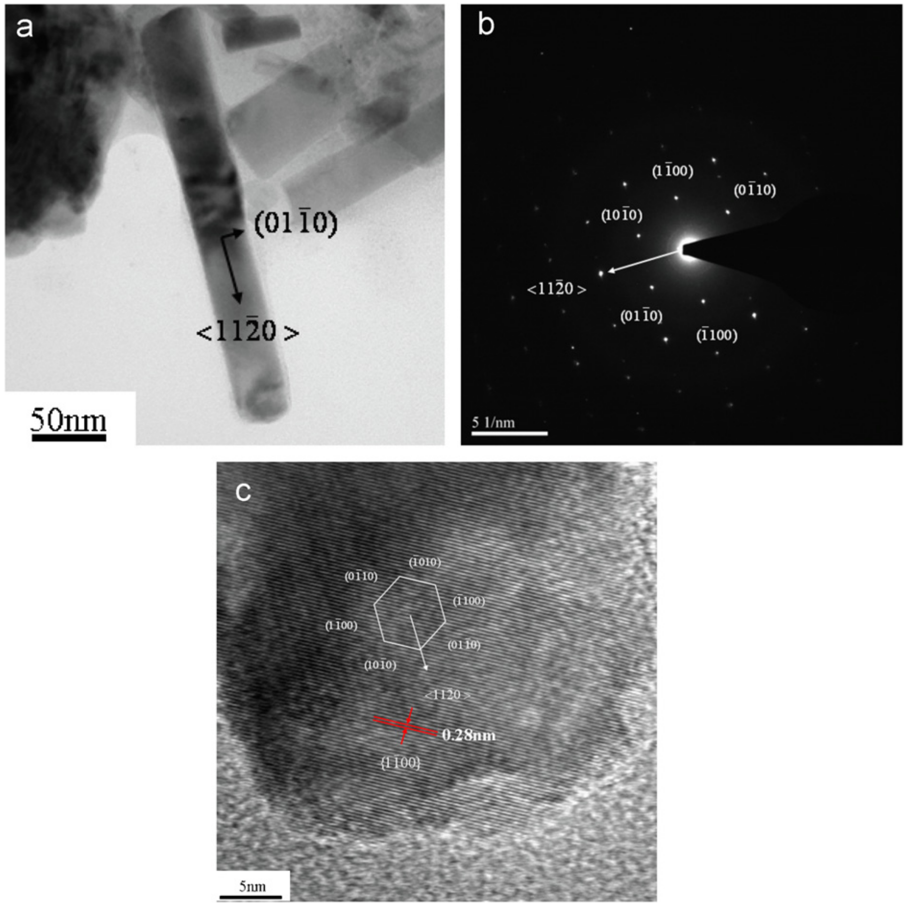

Fig. 3. TEM results of a branched ZnO removed from hierarchical structure: (a) bright-field image, (b) corresponding selected area electron diffraction pattern, and (c) high-resolution electron microscopic image.

$\{01\bar{1}0\}$ plane. The white hexagon in Fig. 3(c) displays the six relevant crystal planes of the branched ZnO nanostructure based on the observed fringes along the three directions. Taken together, it can be concluded that the growth orientation of ZnO nanowhiskers is along $\langle 11\bar{2}0\rangle$, and closed by the $\pm(0001)$ planes on the top and bottom sides [16]. For ZnO single crystals, $\langle 11\bar{2}0\rangle$, $\langle 01\bar{1}0\rangle$, and $\langle 0001\rangle$ are three types of fast growth directions [17], however, the usual growth orientation is $\langle 0001\rangle$. By controlling the growth kinetics, such as, temperature, pressure, and carrier gas, it is possible to change the growth behavior of ZnO nanostructure. The different morphologies of ZnO nanostructures, such as, nanorods [18], nanoplates [19], and nanobelts [20] are formed with different distinct growing directions. One of the most profound factors determining the morphology is the relative surface activities of various growth facets under different experimental conditions. Macroscopically, a crystal has different kinetic parameters for different crystal planes, which are emphasized under the controlled growth conditions. From the energy point of view, it is not favorable to form ZnO nanostructure along $\langle 11\bar{2}0\rangle$ axis. However, it has been reported that the growth direction is decided by the balance between the growth rate and the diffusion of atoms along a given direction [16], i.e., the kinetic factor is the main factor to determine the growth direction. For ZnO nanostructures, it has the biggest area of (0001) planes for the growth direction along $\langle 11\bar{2}0\rangle$ axis. Then, the report depicts that the (0001) planes are suitable for the transport of Zn atoms from the roots to tips [16]; therefore, the orientation for branched ZnO growth could be maintained along $\langle 11\bar{2}0\rangle$ axis.

Results of field-emission characteristics of single-crystalline Zn microtips and hierarchical ZnO structures after annealing treatment are displayed in Fig. 4, obtained at a separation of 30 and 60 μm, respectively. The turn-on electric field for the microtip arrays of Zn is about 33.9 V/μm at a current density of 10 $\mu m/cm^2$, and is enhanced to 8.5 V/μm for hierarchical structures. The obtained field-emission property after annealing treatment is not significantly improved compared with ZnO 1D nanostructures (3.9 V/μm) and hierarchical structures (3 V/μm) obtained by thermal oxidation of brass (CuZn alloy) foil [8,21]. The linear Fowler–Nordheim (FN) behavior (shown in Fig. 4(b)) indicates that the electron emission is proceeded by a field-emission process such as the tunneling of electrons through a potential barrier. The field enhancement factor β is calculated, which is increased from 114 for blank Zn microtips to 3490 for Zn/ZnO hierarchical arrays. The enhancement factor β is related to

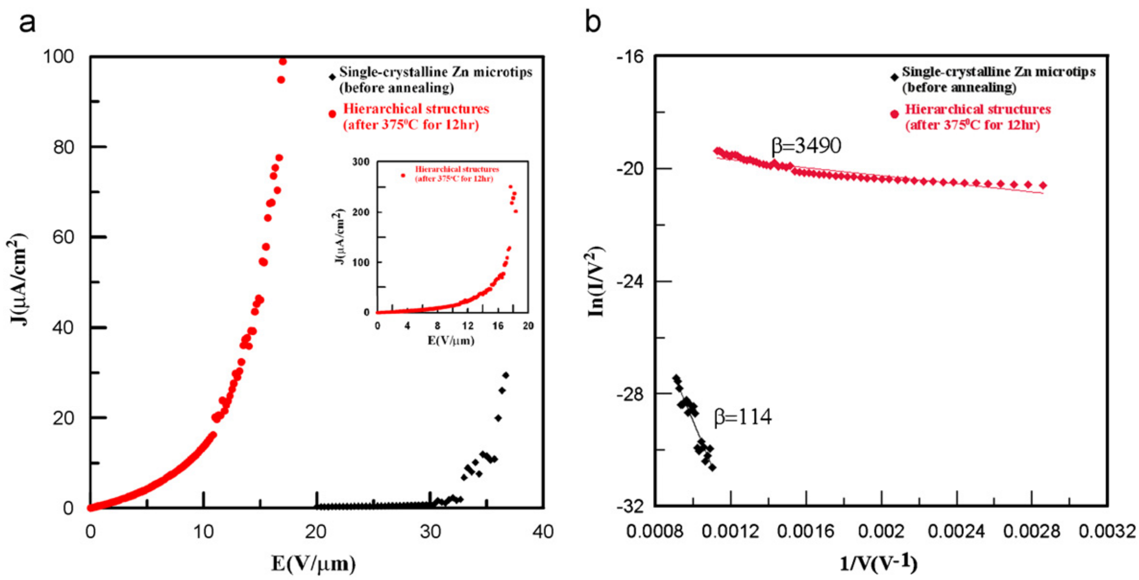

Fig. 4. (a) *J–E* curve of the field-emission property of the hierarchical structures and (b) the FN plot.

emitter geometry and is a function of length, materials crystallinity, morphology, and density of emitters [22]. While the larger enhancement factor interprets that the branched hierarchical structures exhibit more efficient emission sites and superior geometric arrangement. Herein, the estimated field enhancement factor 3490 for Zn/ZnO hierarchical structure obtained in this study is superior to 1D ZnO nanosheets (1600) reported in Chen's result [21], owing to a much larger number of efficient emission sites. The enhancement factor is also superior to the hierarchical structure obtained with gap spacing of 100 (1701) and 200 μm (2127) [8]. Comparing these two hierarchical structures, the better enhancement factor results reported in this present study may be due to the higher aspect ratio (71) of branched nanowhiskers than the branches composed of nanowires and nanosheets [8]. The enhancement factor is better than random deposited tetrapod-like ZnO nanostructures (1941) [23] owing to the more emitter sites, and the 3D hierarchical structures. Besides, the good contact between branched nanostructures and core material should be another crucial factor. Where the good contact can succeed in supplementing electrons from metal tip to emitter sites [24]. In the present study, the direct growth of Zn/ZnO core–shell hierarchical structures on a metallic substrate can provide a naturally good connection between the branching ZnO and the conductive electrode. The good contact results in a lowered energy barrier between metal and semiconductor, i.e., the enhanced electron tunneling phenomenon, and a consequent much better emission property [25]. In summary, the enhancement factor of this hierarchical structure is superior to nanosheets structures, 3D hierarchical morphology, and tetrapod-like nanostructures reported in the literatures. The 3D hierarchical structures in this study have the potential for field-emission application and can be enhanced if the turn-on electric field is further improved.

4. Conclusion

A novel Zn/ZnO core–shelled hierarchical structure has been synthesized by a facile direct annealing method. Herein, the sixfold-faceted Zn pyramid is a fundamental unit for symmetrical self-assembled hierarchical structures with well-defined orientation relationship between Zn and ZnO. However, the growth mechanism for branched ZnO nanowhiskers is owing to stress accumulated at the corner of Zn pyramid surface oxide layer, and then the oxide layer relaxes itself by spontaneous growth. The field-emission performance for the novel nanocharchitectures is enhanced by a much easier electron tunnelling phenomenon from core Zn microtips through Zn/ZnO interface to branched ZnO nanowhiskers. In summary, the preparation and related formation mechanism of the novel hierarchical architectures have been described, and the results obtained open the possibility for applications to functional nanodevice. Besides, the Zn/ZnO core–shelled structure provides not only a good adhesion between stem and branches but also the advantage for in-situ integration into nanodevices.

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