Monotectic growth evolution and raman scattering of self-assembled ZnO hierarchical micro-nanostructures

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Abstract
The self-assembled hierarchical micro-nanostructures with geometric complexity and/or constituent diversity are becoming a promising class of candidates for the next generation nanotechnology. Different from conventional vapor-liquid-solid (VLS) eutectic liquid droplets for one-dimensional (1D) nanowires, the Zn-Bi VLS monotectic liquid droplets are employed to build 1D, 2D and 3D ZnO into 3D hierarchical micro-nanostructures. As-obtained micro-nanostructures are well defined self-assembly and have not yet been observed in the conventional eutectic alloys. The synergy of monotectic droplets and nonthermal equilibrium is responsible for the evolution of ZnO hierarchical micro-nanostructures. Raman spectra show that $E_{2\text{H}}$ and $E_{1\text{L}}$ modes are shifted slightly towards the high-wavenumber side by an amount of 3.7 and 2 cm$^{-1}$ as compared with undoped ZnO nanowires and an additional peak at 519.5 cm$^{-1}$ is associated with Bi$_{38}$O$_{Zn_{60}}$. The results manifest that 3D ZnO micro-nanochitectures possess a bulk phonon structure. The monotectic liquid droplet route presented in this paper may offer a new opportunity to the fabrication of hierarchical nanostructures for realistic technology platforms with multifunctional coupling and interplay.

Introduction
Zinc oxides are well-documented advantageous and representative materials owing to their wide gap of 3.37 eV, large and stable excitonic binding energy (60 meV) at room temperature. As earth abundant, environmentally compatible, properties unique advanced nanomaterials, for over two decades ZnO nanostructures have been arousing great interests and witnessed a rapid development, in which ZnO nanomaterials have been applied for photocatalyst [1], sensors [2], piezo-electronics [3], photonics [4], and photovoltaics [5, 6] based upon the obtained building-blocks nanostructures ranging from one-dimensional (1D) nanowires/nanorods, 2D nanoplates/nanosheets [7] to 3D nanostructures [8, 9]. Driven by fundamental scientific understandings and further advancement of nanotechnology toward the configuration of multifunctional coupling, in recent years, the hierarchical nanostructures assembled by geometric complexity and/or constituent diversity become a promising class of candidates for the next generation nanotechnology [10–12]. The rational integration of different geometric nanostructures and/or dissimilar nanostructures may lead to multiple functionalities, demonstrating unparalleled features. Such hierarchical nanostructures may unearth new opportunities to potentially revolutionize emerging device techniques. Up to now, explosive efforts have been rendered, numerous hierarchical nanostructure materials have been synthesized by various approaches including often-needed templates. However, the cost-effective manipulation of 1D, 2D and 3D nanostructures into hierarchical micro-nanostructures remains a challenge. The eutectic liquid droplet of the VLS mechanism is well suited to control and pattern the growth of nanowires, the eutectic alloys were formed through the absorption of metal catalysts and reactants at high temperature. Little is known for the monotectic liquid droplet to the growth of the nanowires, let alone the monotectic-liquid-droplet-dominated grown hierarchical nanostructures. Long ago,
Yumoto et al used Zn-Bi monotectic liquid droplets around the monotectic point (416 °C) (figure 1) [13, 14] to grow Zn crystal and achieved separated Zn icosahedron (3D), penciled crystal (1D) and disk crystal (2D). The monotectic binary system changes discontinuously at the monotectic point as opposed to the eutectic system. The matrix-rich liquid and impurity-rich liquid are created at similar above and below the monotectic point, respectively. This advantage can be taken to construct hierarchical nanostructures in that the monotectic alloy has the characteristic of separated effect of the growth temperature and concentration upon the morphology. It is hence of scientific interest and significance for the design of hierarchical nanostructures by a monotectic VLS mechanism. The novel ZnO hierarchical micro-nanostructures fabricated from Zn-Bi monotectic system were previously reported [15] by our team but the growth mechanism was not well understood. In this paper, we focus on the formation mechanism of ZnO hierarchical micro-nanostructures fabricated at template-free and relatively low temperature of 500 °C, which can be explained by a combined effect of monotectic system and oxygen introduction. We also investigate the Raman scattering of the self-assembled ZnO hierarchical micro-nanostructures containing nominal Bi₂O₃. The integrated ZnO micro-nanostructures are potentially applicable to micro-nano-varistors due to the existence of the double Schottky barrier. This discussion may provide valuable guidelines and further insights to facilitate the design of hierarchical micro-nanostructures.

**Experimental**

The chemical vapor deposition (CVD) in a horizontal furnace with vacuum pumping system was used and the experimental details were described elsewhere [15]. Briefly, the starting materials were high pure Zn and BiI₃ with the weight ratio of 3:1; the fed gas was high purity of argon gas, the growth temperature was kept at 500 °C, the chamber pressure was maintained at ∼500 Torr, during the annealing at 500 °C, the air was momentarily introduced 3 times (1 min each time) at an interval of 15 min through the outlet end of CVD set-up, the chamber pressure was kept at ∼760 Torr. In order to elucidate the formation mechanism, some additional experiments were carried out as follows: (1) the above-described experiment was conducted without/with the presence of air introduction, and only one time and two times at the same interval; (2) the starting materials are solely Zn in the absence of BiI₃. Field emission scanning electron microscopy (FE-SEM, HITACHI S-4300), and TEM (JEOL JEM 3000F) equipped with energy dispersive x-ray spectroscopy (EDX) were used for the morphological observation and chemical analyses. The Raman backscattering measurements were performed at room temperature using a Spex 1403 Raman scattering spectrometer and a 200 mW Ar⁺ laser at 488 nm as the excitation source.

**Results and discussion**

Figure 2 is the SEM image of as-obtained hierarchical nanostructures. A large quantity of hierarchical nanostructures with well-defined clean and smooth surfaces as shown in figure 2(a) have been obtained. Figure 2(b) exhibits a typical hierarchical nanostructure, which consists of five segments from the bottom to top: (A) truncated icosahedron (polyhedron) (3D) with the height of ∼1 μm; (B) nanorod (quasi-1D) with a length of

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Figure 1. Zn–Bi phase diagram.
800 nm and diameter of 400 nm; (C) a small icosahedron with a height of 400 nm; (D) a smaller nanorod (quasi-1D) with a length of 650 nm and diameter of 200 nm; (E) thin layer-like hexagonal nanodisk (quasi-2D) with a thickness of ∼ 25 nm. The total length of an individual hierarchical nanostructure is approximately 3 μm. The morphology of part (C) is similar to that of the part (A) except for the sizes; the part (D) similar to the part (B) except for the diameter and the length. The hierarchical nanostructures with transparent hexagonal disk-like caps are tilted aligned with respect to the substrates, the facets of the polyhedrons are highly exposed; These results are in agreement with the observation of XRD, an indicative of high quality crystal and probably either exotic mixed or hierarchical structures. Figure 2(c) is the SEM image of polyhedron structures. The samples were acquired from the experiment with initially one-time air introduction and then the samples were shortly taken out from the high temperature furnace. The morphologies are polyhedron (icosahedron) with multiple facets, a clearly visible step and a cap, demonstrating the oriented growth. Figure 2(d) shows the SEM image of the nanostructures fabricated only two-time air introduction with an interval of 31 min from the first time to second time. The nanostructures have the length of approximately 3.2 μm, which are composed of three segments: the bottom (polyhedron) indicated by the red circle, the whiskers, and the hexagonal In contrast to the experiments along with three-time air introduction, there is no small polyhedron in this scenario between the bottom and the cap, which is probably due to the absence of one-time air introduction. Figure 2(e) depicts the SEM image of as-prepared nanowires in the experiment using pure Zn powders starting materials (omitting the BiI3 powder from the precursor). The dominated morphologies are nanowires with length of approximately 10 μm and diameter of 200 nm. These results confirm that BiI3 and air-quench are critical to the formation of self-assembled ZnO hierarchical micro-nanostructures.

Figure 2. SEM image of hierarchical micro-nanostructures. (a) A large quantity of hierarchical nanostructures with well-defined clean and smooth facets; (b) a typical hierarchical nanostructure composed of five segments from the bottom to top: (A) icosahedron (polyhedron) (3D) with the height of ∼ 1 μm; (B) nanorod (quasi-1D) with a length of 800 nm and diameter of 400 nm; (C) a small icosahedron with a height of 400 nm; (D) a smaller nanorod (quasi-1D) with a length of 650 nm and diameter of 200 nm; (E) thin layer-like hexagonal nanodisk (quasi-2D) with a thickness of ∼ 25 nm; (e) the SEM image of polyhedron (icosahedron) structures achieved in the presence of one-time air introduction. (d) the SEM image of the nanostructures fabricated only two-time air introduction with an interval of 31 min; (e) the SEM image of as-prepared nanowires in the experiment in the absence of the BiI3 powder.

Figure 3(a) shows the TEM images of ZnO hierarchical micro-nanostructures. Figure 3(b) depicts the SAED patterns from A area, indicating that there also exist two sets of diffraction spots. One can be indexed to hexagonal structure ZnO with zone axis [2 0 3], other can be assigned to tetragonal β-Bi2O3 with zone axis [142]. ZnO/β-Bi2O3 thus has an orientation relationship with the primary crystallographic planes of ZnO: the (1 1 2 0)ZnO/∥{1 1 0}β-Bi2O3; the (0 0 1)ZnO/∥{0 1 0}β-Bi2O3. Figure 3(c) illustrates a high-resolution TEM image...
of A area, manifesting that crystal phase is mainly composed of ZnO, the interplanar spacing 0.187 nm can be assigned to (10\(\bar{1}2\)) plane of ZnO. As indicated by the square, \(\beta\)-Bi\(_2\)O\(_3\) crystal with 2–4 nm is incorporate into ZnO host matrix. The interplanar spacings of 0.265 nm and 0.314 nm can be ascribed to (102) and (201) plane of \(\beta\)-Bi\(_2\)O\(_3\), respectively. The (102) plane of \(\beta\)-Bi\(_2\)O\(_3\) is in contact with (10\(\bar{1}\)2) plane of ZnO with an angle \(\sim 142^\circ\).

On the other hand, as indicated by the white circle, dislocation is also observed. Figure 3 reveals the high-resolution TEM of B area, besides ZnO host matrix, some nanoparticles and amorphous phase are stacked on the surface of B area. The inset is TEM-EDX of the nanoparticles, exhibiting Zn-Bi alloy with the atomic ratio of 99.41:0.59. Both SAED and HRTEM analyses indicate that the Bi\(_2\)O\(_3\) nanoparticles (2–3 nm) are encapsulated into ZnO. The Bi\(_2\)O\(_3\) encapsulated ZnO hierarchical micro-nanostructure host matrix possess non-linear current-voltage characteristics, which can be used to manufacture chip micro-nano-varistor, protecting micro-nano-circuits [11].

ZnO commonly possesses a hexagonal wurtzite structure, which consists of tetrahedrally coordinated O\(^{2-}\) and Zn\(^{2+}\) ions along the c-axis (figure 4(a)). Typically, ZnO has three kind of preferred growth directions [0001], [10 \(\bar{1}\)0] and [11 \(\bar{2}\)0]. Intrinsically, due to the higher energy of the (0001) crystal surface than other planes, the ZnO crystals have a strong tendency to grow along the [0001] direction. By controlling the growth rates, the three type of morphologies including 1D rod, 2D nanodisk, and 3D polyhedron with predominate crystal facets can be achieved (figure 4(b)). In this work, the three type of structures were configured into ZnO hierarchical

Figure 3. (a) TEM images of ZnO hierarchical nanostructures (b) SAED pattern with two sets of diffraction spots for A area, \('T'\) denotes \(\beta\)-Bi\(_2\)O\(_3\) tetragonal plane. (c) A HRTEM image for A area, the area indicated by rectangle is \(\beta\)-Bi\(_2\)O\(_3\) tetragonal structure; the area indicated by the red circle exhibits dislocation. (d) A HRTEM image for B area, the red circle is \(\beta\)-Bi\(_2\)O\(_3\) with the size of 2–4 nm, and the blue circles are nanoparticles, which are ZnBi alloy as indicated by the inset of TEM based EDX.
micro-nanostructures by means of Zn-Bi monotectic liquid droplets and air quench. The growth processes are schematically described as figure 5.

Process (A): The growth of ZnO polyhedron by a monotectic VLS. Firstly, based on Zn-Bi phase diagram as shown in figure 1, when the temperature reaches above 416 °C of the Zn-Bi monotectic point, Bi stemming from the sublimation of the starting materials BiI₃ mixes with vaporized Zn to form zinc host matrix-rich (∼99at%) Zn-Bi monotectic droplets on the substrate. As the temperature rises to 500 °C, the monotectic droplet becomes larger. Once the air was introduced first time momentarily, Zn inside the droplet can be oxidized to form solid ZnO and subsequently nucleate. The monotectic liquid shape is generally a sphere in that the interface between ZnO crystal surface and the Bi-liquid is non-faceted [14] as shown in the schematic of Process (A). As a small amount of Bi was incorporated into ZnO, which has been verified by TEM-EDX [11], the volume of Bi liquid decreases gradually, and subsequently ZnO grows largely. Now that the growth rate is nearly isotropic, the polyhedron (icosahedron, 38-facet polyhedron, microsphere) can form [16]. Secondly, the moment-introduced air was observed to decrease the growth temperature down to 495 °C. In terms of thermodynamics and kinetics, the descended temperature triggered non-thermal equilibrium of the growth system, and in turn yielded the step and mound shape (figure 2(c)), which is the fingerprint of what is often referred to as the Ehrlich-Schwoebel barrier (ESB) [12]. The activation of atomic processes along the step edge is responsible for the mound, and the facets composed of high index planes arise from the step-faceting mechanism and ESB roughened surface [17–20]. While the temperature of growth system descended, resulting in the reduction of the surface tension of the droplet, the volume of Bi begun to contract and Zn-Bi monotectic alloy preferentially intended towards the top of the icosahedron. The well-defined ZnO icosahedron yielded and the droplet finally located in the c-direction. The growth of icosahedron can be attributed to the screw dislocation driven mechanism evidenced by the step and mound in figure 2(c) and the dislocation in figures 3(c) and (d).

Process (B): The formation of the nanorods. Since Zn-Bi droplets have a good wettability on (0001) plane of ZnO, the interface between (0001) plane ZnO crystal and liquid droplet becomes flat by the effect of a high surface tension, and liquid droplet exhibits a hemisphere, which tends to form rod-like structure. The c direction is Zn-terminated (0001) and the oxygen-terminated (000 1̅) surface. Since the (0001) surface is chemically active while (00 1̅) plane is inert, the growth along [0001] from the Zn-terminated (0001) surface results in the formation of the nanorods. ESB effect indicated that the barrier of (0001) ZnO face has a much higher than that of other faces, at a higher deposition temperature of 500 °C, a large quantity of atoms can be easily captured by ESB. (0001) plane is therefore easy to yield new growth nucleus and form steps and facets,

Figure 4. (a) Crystal structures of hexagonal ZnO; (b) typical 1D, 2D and 3D structures.
Figure 5. Growth schematics of self-assembled 3D ZnO hierarchical micro-nanostructures.
resulting in complicated morphologies with high index facets. The VLS growth in the c direction can continue for a long time until the running-out of oxygen. The nanorod is therefore obtained along the c-axis.

Process (C): The formation of relatively small-size icosahedron. When the oxygen was gradually used up, the nanorod ceased to grow, and the growth system went back to original status of Process (A) but with small size droplet attached on the top of the nanorod. When oxygen was introduced again, the growth analogue to the process (A) occurred again, giving rise to smaller size polyhedron.

Process (D): The formation of the tapered nanorod with hexagonal nanodisk-like cap. This process is much similar to the Process (B). However, in this process, the Zn starting materials were almost used up since the lengths of the nanorods were short with respect to process (B) and the comparative experiment as shown in figure 2(d). The Bi content in droplets becomes richer and richer, whereas Zn content becomes poorer and poorer, the volume of the liquid droplet is extremely little on the (0001) ZnO basal face. The surface tension of liquid decreases and the wettability increases, the droplet has a perfect wetting with ZnO interface, the Bi content is higher and the temperature is still high, the growth rate in the lateral direction is higher than that in the c-axis because of roughening lateral surface [21], the VLS growth can operate in the lateral direction. Finally, the cap was grown with lateral facets, which can be proposed by both wedding-cake growth mechanism and dislocation driven mechanism [20] because of the existence of the dislocation evidenced by HRTEM and nanorod tapered during the growth.

Process (E): The formation of high quality ZnO hierarchical micro-nanostructures. Prior to third-time oxygen quench, the growth process has completed. However, the oxygen in this scenario plays a role on annealing the sample and enhanced the crystal quality, which has been verified by PL [11].

By the synergy of Zn-Bi monotechnic droplets, oxygen introduction, the conventional separated 3D micro-icosahedron, 1D nanorods and 2D hexagonal nanoplates separated nanostructures were assembled into high quality ZnO hierarchical micro-nanostructures based on a combined mechanism of both wedding cake mounds driven by 1D and 2D nucleation and spirals driven by screw dislocation.

Raman scattering is sensitive to the microstructure of nanosized materials. It is also used here to clarify the structure of ZnO based nanoarchitecture. Figure 6(a) shows the Raman spectrum under excitation of a 488 nm laser line. The peaks at 323 cm$^{-1}$, 387 cm$^{-1}$ and 435 cm$^{-1}$ and 581 cm$^{-1}$ are assigned to E2H-E2L, A1T, E2H and E1L mode of the ZnO modes, respectively. The peak at 510 cm$^{-1}$ can be assigned to the contribution from Si since the substrate is probably an oxidized Si [22]. Figure 6(b) shows a typical Raman spectrum of ZnO based nanoarchitecture. The peaks at 334 cm$^{-1}$, 381 cm$^{-1}$, 4387 cm$^{-1}$, and 583 cm$^{-1}$ are assigned to E2H-E2L, A1T, and E2H and E1L of the host ZnO modes. One can easily see the characteristic of the wurtzite phase from the E2H. However, the peak at 519.5 cm$^{-1}$ is not well understood. With reference to our previous work [11], all the data of the XRD, SAED, HRTEM and PL articulated the Bi and/or oxides have been incorporated to ZnO host matrix. The peak at 519.5 cm$^{-1}$ is close to the peak at 527 cm$^{-1}$ in bismuth oxides, which was ascribed to Bi$_{30}$ZnO$_{60}$ [23]. The peak was shifted to low wavenumber side with 7.5 cm$^{-1}$. As a comparison with the Raman spectrum of pure ZnO nanowires, the peaks at 438.7 cm$^{-1}$ and 583 cm$^{-1}$ are shifted slightly towards the high-wavenumber side by an amount of 3.7 and 2 cm$^{-1}$, indicating that ZnO hierarchical micro-nanoarchitecture features a bulk structure.
Conclusions

In summary, the Zn-Bi VLS monotectic liquid droplets are initiated to assemble 1D, 2D and 3D ZnO micro-nanostructures into 3D ZnO hierarchical nanostructures with a high surface area. The novel nanostructure configuration is well defined, self-assembled and rare. The interplay of monotectic droplets, Ehrlich-Schwoebel barrier and nonthermal equilibrium are involved in the growth of ZnO hierarchical micro-nanostructures. Raman spectra manifest that 3D ZnO micro-nanoarchitectures contains Bi related compound, which potentially possess a promising application for micro-nano-varistors. The monotectic VLS may offer new opportunities to the advancement of hierarchical micro-nanostructures towards multifunctional coupling materials and devices.

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