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# Self-assembled Growth and Photoluminescence of Leaf-like Zn/ZnO Microstructure by Thermal Evaporation Method

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**Abstract** The novel 2D leaf-like zinc dendritic structures have been synthesized on ZnO buffer layer coated onto Si substrates. The growth process is described as free-catalyst, self-assembly and vapor-solid growth mode. The length of the Zn dendrite is about dozens of micrometers and its thickness is about 200 nm. The fastest growth direction of the dendrites is along the carrier gases downstream direction to release the latent heat of solidification. After the zinc dendrites have the thermal process in oxygen ambient, the slim and uniform ZnO nanowires are grown on the surface of Zn dendrites. The results of XRD analysis indicated that the ZnO nanowires are with a hexagonal wurtzite structure. The growth mechanisms of Zn/ZnO structures were investigated. The PL spectrum of Zn/ZnO dendritic structures shown that a weak UV near-band-edge emission is at 380 nm and a strong green emission is centered at 505 nm. The green emission is attributed to radiation transition of donor-acceptor pair.

**Key words**: thermal evaporation; zinc oxide; microstructure; photoluminescence
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## 1 Introduction

ZnO, which has a large band-gap energy of 3.37 eV and higher exciton binding energy of 60 meV at room temperature, has been paid great attention for its potential applications in UV laser, optoelectronics, piezoelectric transducer, acoustic wave source, gas sensor, and so on[1,2].

Low-dimension ZnO nanostructure-materials with novel morphology have unique physical properties used in nano-devices. Recently, ZnO nanostructures with various morphologies, such as nanowires, nanobelts, nanotubes, nanocombs, nanosprings, and nanodendrites, have been fabricated and its special properties have been also extensively researched[3~11].

Among these novel nanostructure-morphologies, nanodisks have attracted much attention for their potential applications in information storage media and nanosensor. The electrochemical dendritic growth of zinc has been studied using aqueous media[12,13]. Our interest in zinc dendritic structures is to fabricate high-performance polycrystalline electrodes.

Here, a simple thermal evaporation was adopted to synthesize Zn dendrites microstructures. Then, the sample was annealed in the oxygen ambient, ZnO nanowires were grown on the surface of the Zn dendrites. The Zn/ZnO structures were fabricated. The growth mechanisms related with morphologies were investigated in the vapor phase growth process. The zinc dendrites microstructures were obtained under non-equilibrium conditions, the growth mechanisms were discussed with the view of surface kinetics and thermodynamics. The influence of the temperature field on vapor saturation ratio was also taken into consideration in discussion. The photoluminescence properties related with defects were discussed in detail.

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## 2 Experimental Section

The Zn dendritic structures were synthesized by a simple thermal evaporation and vapor-phase deposition process in a horizontal tube furnace. The 99.999% Zn powder was loaded in quartz boat as the source, which was placed in the center of the horizontal tube furnace. A piece of Si substrate covered a thin layer of ZnO deposited by thermal evaporation method was placed downstream 20 cm position apart from the source. At the position, the great temperature gradient can be obtained and the lattice mismatch between Zn and Si substrates can be decreased. Ar gas was as the carrier gas with a flow of 100 sccm, and 10 min later, the furnace was heated at a rate of 30 ℃/min and kept at 680 ℃ for 1 h. The temperature of the substrate was about 200 ℃. During the fabrication process, the pressure in the tube was kept at constant pressure. After the temperature of the furnace was naturally cooled to the room temperature, a layer of white-gray deposits with metal luster were obtained on the substrates. The structure and morphology of the obtained deposits were characterized by a field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS), and X-ray diffractometry. The micro-PL spectra were measured with excitation wavelength of 325 nm.

## 3 Results and Discussion

Fig. 1(a) shows Zn dendrites have remarkable layered structures. The Zn dendritic structures are similar to the branches of a tree, which is made up of the stems and subbranches. The sub-branches grow along two sides of the stem with perfect symmetry. The angle is about 60° between the stems with the subbranches, which have the same dendritic structures. The width of a single subbranch of the Zn dendrites is about 10 μm and its length is about dozens of micrometers. Moreover, each subbranch is composed of numerous Zn nanodisks with hexagonal structure.

Fig. 1(b) shows the low magnification SEM images of the sample annealed in $O_2$ ambient. The

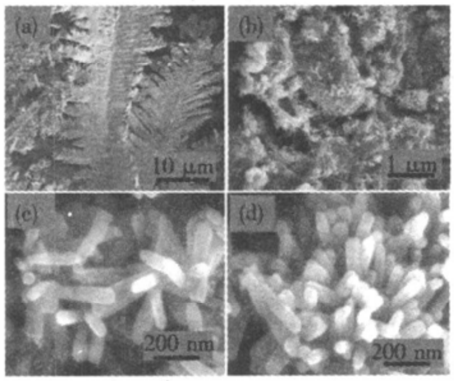


Fig. 1 The SEM images of Zn dendries (a) as-grown; (b) low magnification SEM image of the sample annealed in $O_2$; (c) and (d) high the image of the sample annealed in $O_2$.

annealed sample looks like corals, the Zn dendrites are covered with a layer of slin fibers. Fig. 1(c, d) show the high magnification SEM images of the samples annealed in $O_2$ ambient. The slin and uniform nanowires are observed on the surface of the Zn dendrites. The diameter of nanowires is about 30 nm and its length is about 200 nm. EDX measurement was carried out to analyze the components of the sample.

Fig. 2 shows the EDX pattern of the as-grown and annealed samples, respectively. EDX analysis shows that an oxygen peak at 0.53 eV and Zn signals at 1.00, 8.63 and 9.58 eV are all observed. It illustrates that the sample is only composed of zinc and oxygen elements. The ratio of zinc to oxygen is about 88∶12 of the as-grown sample. It suggests that the surface of the Zn dendrites are oxidated by trace oxygen in Ar carrier gas. As the sample was annealed in oxygen ambient, the ratio of zinc to oxygen is about 73∶27. It suggests that a thin layer of ZnO is formed on the surface of Zn dendrites. Fig. 3 shows the XRD pattern of the samples. XRD analysis shows that the diffractive peaks of as-grown at 36.37°, 39.20°, 43.41° and 54.52° are observed. These diffractive peaks are assigned to Zn diffractive peaks with (201), (202), (203) and (300) orientations, respectively. The results of XRD indicate that the Zn dendrites can be attributed to the hexagonal wurtzite structure. As the sample annealed in $O_2$ ambient at 350 ℃ for 2 h, the peak at 36.37° is split to two peaks, one is at 36.2° and the other is at 36.37°. As well known, the diffractive peak at 36.2° is the diffractive peak of bulk ZnO with (101) orientation. It suggests that Zn/ZnO structures have been synthesized. The intensity of diffractive peaks of annealed sample turned weak. It is attributed to Zn consumption and ZnO formation.

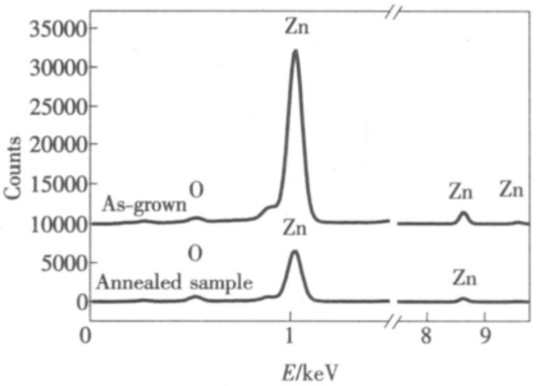


Fig. 2 The EDX spectrum of the as-grown and annealed sample, respectively.

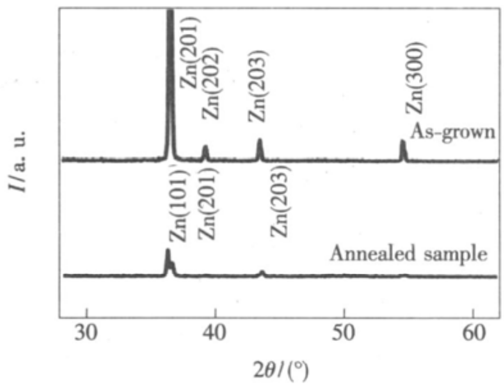


Fig. 3 The XRD pattern of the as-grown and annealed sample, respectively.

The possible formation mechanism of the Zn/ZnO structures can be depicted as follow: During the growth process, the Zn supersaturation evaporation vapor was formed as the temperature reached 680 ℃, which was transported by the Ar carrier gas. When the supersaturation Zn vapor flowed along the downstream, the metal Zn was separated out and deposites on the substrates for the great temperature gradient at the downstream deposition-area. The Zn dendrites growth may be along three crystal axis directions to release latent heat of solidification. The nanodisks grow and fuse together along one crystal axis direction, which is along downstream direction, to form the stem of Zn dendrites. During the growth process, the nanodisks were grown out along the edges of {01$\bar{1}$0} facets[14], which were with a lot of tiny convexes due to uneven release latent heat of solidification. These tiny convexes can form abundant crystalline interfaces with fairly high surface energy, which tend to adsorb Zn ions to lower the system energy. To increase the surface area of (0001) plane, it can release fastly the latent heat of solidification due to (0001) plane with high surface energy. Therefore, the lateral growth of the group of {01$\bar{1}$0} facets was preferred. The subbranches growth is along the two side of the stem. The angle is 60° between the subbranches with the stem, the whole Zn dendritic structures were formed. As the sample was annealed in $O_2$ ambient, ZnO shell layer was generated. The ZnO nanowires growth is a homo-epitaxy growth process. The homo-nucleation is with a relative less formation energy. The tiny nucleus would be induced on ZnO (0001) plane, which was the most active area due to high concentration of dangling bonds. Moreover, the high vapor saturation ratio was preferred by linear growth. Therefore, a lot of ZnO nanowires were obtained.

Fig. 4 shows the XPS spectra of ZnO nanowires. The peak at 530 eV is attributed to O1s binding energy. The peaks at 1 020 and 1 045 eV are attributed to Zn $2p_{3/2}$ and $2p_{1/2}$ binding energy, respectively. The XPS quantitative analysis results show that the elemental atomic ratio of Zn∶O is 31∶69. The nonstoichiometric component suggests that the existence of Zn vacancies and /or oxygen interstitials in ZnO nanowires.

Fig. 5 shows the room temperature PL spectraum of Zn/ZnO nanostructures. A weak UV near-band-edge emission at 380 nm was observed and a strong green emission is centered at 505 nm. It is traditionally

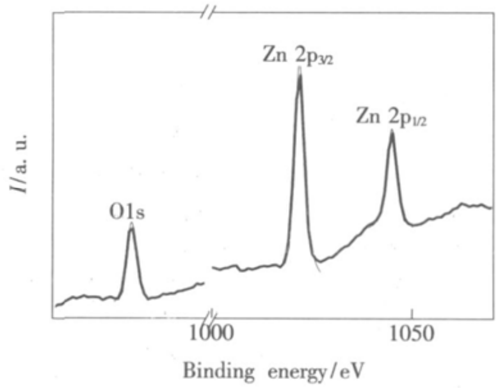


Fig. 4 The XPS spectrum of ZnO nanowires

deemed that the green emission originated from the recombination of the holes and electrons occupying the singly ionized O vacancy. However, in our experiment, it is reasonable that there exists interstitial oxygen and zinc vacancy in ZnO lattice, even as the dominant intrinsic defect, since the ZnO are formed in $O_2$ ambient. During thermal oxidation process, a decrease of the Zn pressure can result in an increase of Zn vacancies[15]. In our experiment, the weak UV NBE emission is attributed to the abundant surface trapping states, which can trap the excited electrons and depress the electron radiative transition[16], the strong green emission is attributed to the intrinsic defects, such as zinc vacancy, interstitial oxygen and antisite oxygen defects. The strong green emission is attributed to the transition from the shallow donor to the deep acceptor ($V_{Zn}$, $O_i$ or $O_{Zn}$). The interstitial Zn is at 0.05 eV below the conduction band. Moreover, the unidentified defects, which can be as the shallow donor, are at 0.10, 0.12, and 0.29 eV below the conduction band. In our experiment, the green emission is explained as the transition of donor-acceptor pair.

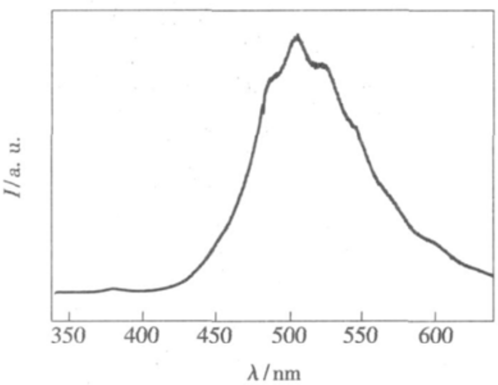


Fig. 5 The room temperature PL spectrum of Zn/ZnO dendritic structures

## 4 Conclusion

The leaf-like Zn dendrites were synthesized by a simple thermal evaporation Zn powders method. The Zn dendrites are the hexagonal wurtzite structure by the XRD pattern analysis. The stem of the Zn dendrites grows along the downstream direction to release latent heat of solidification at the deposition-area with a high temperature gradient. Moreover, the tiny convexes on the facets with fairly high surface energy tends to adsorb Zn ions and promote the preferred growth of the nanodisks. The subbranches have a relative lower growth velocity than that of the stem. Therefore, the leaf-like Zn dendrites are formed. As the sample is annealed in $O_2$ ambient, ZnO nanostructures were formed. ZnO nanowires were preferential to growth due to the vapor with a high saturation ratio. The control of supersaturation is a prime consideration in obtaining Zn dendrites and ZnO nanowires. It illustrates that the degree of supersaturation determines the prevailing growth morphology. The PL spectrum shows that a weak UV NBE emission and a strong green emission are observed. The weak UV NBE emission is attributed to the surface trapping states effect. The strong green emission is related with the high concentration of intrinsic defects, such as Zn vacancies and oxygen interstitials. The green emission is explained as the radiative transition of donor-acceptor pair.

## References

[1] Yu S F, Yuen C, Lau S P, *et al*. Ultraviolet amplified spontaneous emission from zinc oxide ridge waveguides on silicon substrate [J]. *Appl. Phys. Lett.*, 2003, **83**(21): 4288-4290.

[2] Moon T H, Jeong M C, Oh B Y, *et al*. Chemical surface passivation of $HfO_2$ films in a ZnO nanowire transistor [J]. *Nanotechnology*, 2006, **17**(9): 2116-2121.

[3] Lin Y R, Yang S S, Tsai S Y, *et al*. Visible photoluminescence of ultrathin ZnO nanowire at room temperature [J]. *Cryst. Growth & Des.*, 2006, **6**(8): 1951-1955.

[4] Kong X Y, Wang Z L. Spontaneous polarization-induced nanohelixes, nanosprings, and nanorings of piezoelectric nanobelts [J]. *Nano Lett.*, 2003, **3**(12): 1625-1631.

[5] Tong Y H, Liu Y C, Shao C L, *et al*. Growth and optical properties of faceted hexagonal ZnO nanotubes [J]. *J. Phys. Chem. B*, 2006, **110**(30): 14714-14718.

[6] Pan Z W, Mahurin S M, Dai S, et al. Nanowire array gratings with ZnO combs [J]. Nano Lett., 2005, **5**(4): 723-727.

[7] Zhang X Y, Dai J Y, Lam C H, et al. Zinc/ZnO core-shell hexagonal nanodisk dendrites and their photoluminescence [J]. Acta Mater., 2007, **55**(15): 5039-5044.

[8] Li C, Fang G J, Liu N S, et al. Snowflake-like ZnO structures: Self-assembled growth and characterization [J]. Mater. Lett., 2008, **62**(12-13): 1761-1764.

[9] Cheng Wende, Wu Ping. Synthesis and strong blue light emission properties of ZnO tetrapod nanostructure [J]. Chin. J. Lumin. (发光学报), 2006, **27**(4): 608-613 (in Chinese).

[10] He Ying, Wang Jun'an, Sang wenbin, et al. Self-assembling oriented growth and optical properties of ZnO nanowires via polymer soft-template [J]. Chin. J. Lumin. (发光学报), 2006, **27**(5): 766-772 (in Chinese).

[11] Dong Jingbing, Cheng Yao, Wan Jianguo, et al. Preparation and characterization of tin catalysted ZnO twin-crystal nanowires [J]. Chin. J. Lumin. (发光学报), 2006, **27**(5): 777-781 (in Chinese).

[12] Lopez C M, Choi K S. Electrochemical synthesis of dendritic zinc films composed of systematically varying motif crystals [J]. Langmuir, 2006, **22**(25): 10625-10629.

[13] Li G R, Lu X H, Qu D L, et al. Electrochemical growth and control of ZnO dendritic structures [J]. J. Phys. Chem. C, 2007, **111**(18): 6678-6683.

[14] Wang X D, Song J H, Wang Z L. Single-crystal nanocastles of ZnO [J]. Chem. Phys. Lett., 2006, **424**(1-3): 86-90.

[15] Heo Y W, Norton D P, Pearson S J. Origin of green luminescence in ZnO thin film grown by molecular-beam epitaxy [J]. J. Appl. Phys., 2005, **98**(7): 073502-1-6.

[16] Zeng H B, Liu P S, Cai W P, et al. Aging-induced self-assembly of Zn/ZnO treelike nanostructures from nanoparticles and enhanced visible emission [J]. Cryst. Growth Des., 2007, **7**(6): 1092-1097.

# 热蒸发法 Zn/ZnO叶状微米结构自组装生长及其发光特性

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**摘要:** 采用热蒸发法在 ZnO缓冲层覆盖着 Si衬底上合成了 2D叶状的 Zn晶枝结构, Zn的晶枝长度约为几十微米, 厚度约为 200 nm, 随后 Zn晶枝在 $O_2$ 的气氛下热处理, 在晶枝表面获得纤细、均匀的 ZnO纳米线。晶枝按照无催化、自组装、汽相生长模式生长, 晶枝最快生长方向是沿着载气气流的方向释放凝固潜热, XRD分析结果结果显示了 Zn纳米线具有六角纤锌矿结构, Zn/ZnO的发光谱显示, 在 380 nm处有一弱的 UV近带边发射和中心在 505 nm处的强绿光发射, 绿光发射归因于施主-受主对之间的辐射跃迁。

关　键　词: 热蒸发; 氧化锌; 微米结构; 光致发光

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