Research Article

Growth and Structure of Pure ZnO Micro/Nanocombs

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Comb-shaped ZnO micro/nanostructures were grown on copper substrate using a highly repeatable catalyst-free chemical vapor deposition method. The structure of the ZnO micro/nanocombs was analyzed, and the necking-down phenomena of the comb teeth was explained. The cathodoluminescence (CL) spectrum was measured on an individual ZnO comb, and a strong deep-level emission centered at about 520 nm was observed.

1. Introduction

ZnO, with a wide bandgap of 3.37 eV at room temperature and a high exciton binding energy of 60 meV, is a direct bandgap II–VI semiconductor with good performances. In the past decade, nano-ZnO has attracted considerable attention. A variety of ZnO nanostructures, nanowires [1], nanorods [2], nanoribbons [3], nanocombs [4], nanorings [5], nanohelices [6], and nanotetrapods [7], and have been discovered and reported. Among them, ZnO nanocombs consisting of a ribbon and an array of parallel nanorods perpendicular to the ribbon are of interest for nanocantilever arrays [4], laser arrays [8], nanocomb biosensors [9], and gratings [10].

So far, ZnO nanocombs have been synthesized mainly by thermal evaporation using Zn or ZnO usually mixed with graphite powers as precursors in a wide temperature range (440°C–1350°C) [4, 11–18]. In most cases, Au was also used as the catalyst in the growth. The mechanism involved in generating ZnO nanocombs includes vapor-solid (VS) mechanism without any catalysts and vapor-solid-liquid (VLS) mechanism directed by catalysts. Wang et al. [4] reported that the Zn-terminated (0001) polar surface is chemically active and can initiate a self-catalyzed effect that promotes the growth of comb-like arrays, while the O-terminated (000 $\bar{1}$) polar surface is inert in initiating growth. Chen et al. [16] reported that both VS and VLS mechanisms could explain the growth of ZnO comb-like structures.

Herein, a chemical vapor deposition (CVD) process using a precursor of mixed ZnO and graphite powders is carried out to grow comb-like ZnO micro/nanostructures. In the process, no catalyst is used and as well no catalyst particle is detected at the comb tip, indicating a VS mechanism in the growth of the ZnO comb-like structures. The absence of catalyst particle on the as-grown ZnO micro/nanocombs is an advantage to fabricate ZnO micro/nanodevices without the influence of impurity. This facile way for growing pure ZnO comb-shaped micro/nanostructures on a large scale will facilitate the broad applications of ZnO micro/nanocombs. At last, the structure and growth mechanism of the comb-shaped ZnO structures were discussed, and the CL properties of individual ZnO combs were investigated.

2. Experimental Section

The ZnO micro/nanocombs were synthesized in a tube furnace system [19] through a chemical vapor deposition (CVD) method. At first, a mixture of ZnO and graphite powders (weight ratio 2 : 1) was grounded and loaded into a quartz boat, which is placed at the center of a horizontal tube furnace. A clean Cu sheet without catalyst was used as a substrate and placed downstream of the source materials to collect the products. Argon, with a flow rate of 30~70 sccm (standard cubic centimeters per minute), was used as the carrier gas. Then, the source materials were heated up to 1000°C with a heating rate of 45°C/min. The substrate

FIGURE 1: XRD pattern of as-prepared ZnO comb-like structures grown on Cu substrate.

temperature is 950°C due to the temperature gradient of the tube-furnace. The pressure was kept at 1 atm during the reaction. The growth was maintained for 90 min. Then, the furnace was cooled down to room temperature, and white products were found covering the Cu substrate.

The as-synthesized products were characterized by X-ray diffraction (XRD, Panalytical X'pert PRO diffractometer), scanning electron microscopy (SEM, Hitachi S-4800), energy-dispersive X-ray (EDX) spectroscopy and transmission electron microscopy (TEM, Tecnai G² F20 U-TWIN). Cathodoluminescence spectrum of an individual comb-like structure was recorded using an in situ optical-electrical measurement system based on a Keithley 4200 semiconductor characterization system and an FEI XL30-SFEG SEM equipped with 4 Kleindiek MM3A nanomanipulators, and the current intensity of electron beam was less than 1 nA. More details about the in situ optical-electrical measurement system can be found in [20].

3. Results and Discussion

X-ray powder diffraction pattern of the as-synthesized ZnO micro/nanocombs was shown in Figure 1. Reflections from wurtzitic ZnO could be readily identified and a strong preferred orientation of (101) plane was evidenced. Some weak reflections corresponding to Cu, Cu₂O, and CuO were also observed and ascribed to the Cu substrate.

Figure 2 is an energy-dispersive X-ray spectrum measured on the comb-like structures, and it reveals that only Zn and O can be detected and Cu or other elements are absent. Therefore no particles of Cu, Cu oxides, or Cu alloys contaminate the comb-shaped structures; the Cu, Cu₂O, and CuO identified by XRD should come from the substrate.

Typical SEM images are given in Figures 3(a)–3(c). Some ZnO comb-shaped structures accumulating over the

FIGURE 2: EDX spectrum of the ZnO comb-like structures.

substrate can be seen from Figure 3(a). Figure 3(b) presents the details of the morphology of an individual ZnO comb. The comb-like structure has teeth with a length up to 20 μm and a thickness of several hundreds of nanometers. All the teeth stand parallel to one another on one side of ribbon-like stems. The stems are ribbons with a thickness of several hundreds of nanometers and a length of several tens of micrometers. The width of the ribbon is almost the same along the growth direction, which is different from the blade-like structures reported in previous literature [11, 16]. Shown in Figure 3(c) is another kind of ZnO comb-like structures forming on the Cu substrate. The width of the tooth shrinks drastically from several μm at its root to about 300 nm at its sharp tip. The teeth are uniform in length and width in general. The distance between two adjacent teeth is about 2 μm.

The ZnO micro/nanocombs were further characterized by TEM. Shown in Figure 4(a) is a low-magnification image of a comb-like ZnO structure, and the selected area electron diffraction (SAED) pattern obtained from the stem part of the comb-like structure is given as an inset. Presented in Figure 4(b) is an image of the root part of the teeth at higher magnification and SAED pattern taken from a tooth. The identical SAED patterns obtained from different parts of the comb-like structure indicates that the entire particle is a single crystal. SAED patterns agree well with [100] zone axis of wurtzitic ZnO, confirming the results of XRD and EDX analyses. Though [001] cannot be distinguished explicitly from [00 $\bar{1}$] direction with only SAED pattern, we assume that the direction from stem ribbon to the tip of the tooth is [001] in reference to [4]. The teeth of the comb-like structure grow along *c*-axis while the stem ribbon grows along [120] direction with (2 $\bar{1}$ 0) planes as top and bottom surfaces. Different from the comb structures reported here, the stem ribbons of comb-like structures synthesized by Wang et al. grow along [100] direction with (010) planes as top and bottom surfaces. The necking down of the teeth is frequently observed for our comb-like structures, and interestingly, the positions of necking down are quite uniform for teeth of the

FIGURE 3: Typical SEM images of the comb-like ZnO structures.

FIGURE 4: (a) TEM image of a ZnO comb, showing the distinct arrays of teeth on one side. The inset is the SAED pattern taken from the stem ribbon. (b) TEM image of the root part of the teeth at higher magnification and the corresponding SAED pattern. (c) Schematic models of the comb-like structure observed by TEM. (d) A projection of wurtzite-type ZnO along $[100]$ direction highlighting its polar planes (001) , (011) , and $(0\bar{1}1)$.

same comb-like structure. The inclined facets occurring at the place where the teeth are necking down are $(0\bar{1}1)$ and/or (011) , as shown in Figures 4(b) and 4(c). It is noteworthy that $(0\bar{1}1)$ and (011) are polar planes, as indicated in Figure 4(d). We suggest that the necking down of the teeth is closely related with the polar planes of wurtzite-type ZnO. Possibly, the surface energy of $(0\bar{1}1)$ and (011) polar planes are comparable with that of (001) , the most well-known polar planes for wurtzite-type structure. Fluctuation of experimental conditions during the growth can lead to that $(0\bar{1}1)$ and (011) surfaces are energy preferred over (001) . Then, $(0\bar{1}1)$ and/or (011) facets will appear at the tips of the teeth. Clearly, nonpolar surfaces with low indices, such as (010) and $(2\bar{1}0)$ as well as their equivalents are more stable than polar ones. Hence, non-polar surfaces are preferred over

polar ones to terminate the single crystalline teeth during the subsequent growth. When such a process happens, a necking down of the teeth will result, and sharper tips will be obtained. So the necking-down phenomena dominated by competition between polar surfaces and non-polar ones can be utilized to synthesize wurtzite-type structures with both sharp tips at nanoscale and thick roots in size of micrometers, which should be very desirable for some applications.

The CL spectrum measured on an individual ZnO comb-like structure is shown in Figure 5. Only a broad and strong green emission band centered at 520 nm is observed, which is commonly seen in ZnO materials synthesized under oxygen-deficient conditions, such as the gas-phase produced nanowires [21]. The chemical and structural origins of the green luminescence from undoped ZnO are

FIGURE 5: CL spectrum measured on an individual ZnO comb-like structure.

still a matter of debate [22, 23]. In what is perhaps the most frequently cited explanation, electrons trapped in singly ionized oxygen vacancies recombine with valence band holes [24]. In another frequently cited explanation, electrons in the conduction band and/or shallow donor states recombine with holes that have been trapped in oxygen vacancies [25]. Compared to the strong green emission centered at 520 nm, no near band edge emission of ZnO was found in Figure 5. The disappearance of the near ultraviolet (UV) band edge emission is due to the low electron beam (1 nA) of the CL measurement. Such a low electron beam generates few electron-hole pairs. Furthermore, a large number of excited electrons are trapped by oxygen vacancies, resulting in little recombination of electron-hole pairs. Thus, the near band edge emission peak of ZnO disappears.

4. Conclusions

In summary, ZnO micro/nanocombs have been successfully synthesized on Cu substrate without catalyst using a simple CVD method. The growth of the comb-like structures can be attributed to a VS mechanism. The structure of the ZnO micro/nanocombs was analyzed and the necking-down phenomena of the comb teeth was explained. The CL spectrum was measured on an individual ZnO comb and only a broad strong green emission band was observed. This facile way for growing pure ZnO micro/nanocombs on a large scale will facilitate the broad applications of ZnO micro/nanocombs.

Authors' Contributions

T. Xu and P. Ji have equally contributed to this paper.

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