Formation of double-side teethed nanocombs of ZnO and self-catalysis of Zn-terminated polar surface

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Abstract

Polar surface induced asymmetric growth of single-side teethed ZnO nanocombs was attributed to the self-catalysis of the Zn-terminated (0001) surface (Z.L. Wang, X.Y. Kong, J.M. Zuo, Phys. Rev. Lett. 91 (2003) 185502). In this Letter, nanocombs of ZnO with double-sided teeth have been observed. This symmetric growth of the fish-ribbon like teeth has been identified due to the existence of an inversion domain boundary along the ribbon, so that both side surfaces of the ribbon are terminated with the chemically active Zn-(0001) plane. A model is also given about the formation of \( \{110\}\) double-sided nanocombs based on the nucleus composed of multiply twinned pyramids. The data show that the Zn-terminated (0001) surface is responsible for the formation of the teeth, while the oxygen-terminated (0001) surface is chemically inactive and does not grow teeth.

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(FE-SEM, field emission LEO 1530 FEG) and transmission electron microscopy (TEM, field emission TEM Hitachi HF-2000).

Fig. 1a is a low magnification SEM image of the as-grown single-sided ZnO combs with asymmetric teeth distribution [8–12]. The yield of the nanocombs is ~100%. A typical nanocomb is magnified and is inserted, showing many thin teeth of similar lengths and diameters growing out of a straight primary ribbon. These teeth have spacing around 200 nm, diameter ~50 nm and length ~2 μm. Fig. 1b is another configuration for the single-sided combs, in which a row of hexagonal nanowires with two segments of different diameters stacking one on the other along the length direction. From the hexagonal symmetry of the nanowire, its growth direction is [0001]. Fig. 1c shows a comb structure with a series of long thin belts (40–50 μm in length, 0.5–4 μm in width), growing in parallel out of one side of the ribbon and forming a ‘waterfall-like’ configuration. In Fig. 1d, the nanocombs have a set of much wider teeth, with a wide range of inter-teeth spacing, a length from 1 to 5 μm and a width of 200–500 nm. The upper inset image reveals the quasi-rectangular shape of the cross section of the teeth. Fig. 1e is a TEM image of a typical single-sided comb structure and the corresponding electron diffraction pattern. The diffraction pattern shows that the growth direction of the teeth is [0001] and of the primary ribbon is [2110], and both share the same top and bottom surfaces of ±(0110).

The formation of one-sided asymmetric nanocombs has been attributed to the self-catalysis effect of polar surface

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Fig. 1. (a) As-grown, single-side teethed ZnO comb structures. Inset is a magnified image of a single-sided comb; (b) to (d) are SEM images of single-sided combs with different morphologies. (e) A typical TEM image of the single-sided nanocomb. Inset diffraction pattern is from the circled area showing that the growth direction of the teeth is [0001].
Due to the non-central symmetric characteristic of ZnO, the (0001) of ZnO is terminated with Zn cations, and the (0001) is terminated with oxygen anions, which are the two typical polar surfaces of ZnO, and they induces a group of unique nanostructures [13]. The Zn-(0001) surface is chemically active and its self-catalysis results in the growth of teeth on one side. The oxygen terminated (0001) surface is relatively chemically inert and produces no growth. This is the reason that the asymmetric nanocombs are most frequently received [8–12], and they can be grown almost at 100% purity.

However, symmetric nano-combs with double-sided teeth (fish-ribbon type) have also been produced in our synthesis, and sometimes the yield can be more than 80%. In Fig. 2a, a low magnification SEM image shows a high yield of the double-sided teeth comb structure. Fig. 2b is a magnified image of a symmetric comb, which clearly displays that the teeth grow from both sides of the ribbon. Fig. 2c is another type of double-sided combs with two rows of dumbbell-like shaped teeth.

The formation of the symmetric nano-combs cannot be explained by the polar surface model if the main ribbon is a single crystal with both sides of the combs being terminated by Zn-(0001) and O-(0001), respectively. To find out the formation process of the double-sided nano-combs, we have used convergent beam electron diffraction (CBED) to determine the polarity of the two sides. Fig. 3a is a low magnification TEM image from the nano-comb, displaying a symmetric distribution of the teeth at both sides of the ribbon. The corresponding electron diffraction pattern recorded from a group of teeth is given in Fig. 3b, showing the conventional spotty pattern of [010], but there is a radial angular twist profile as indicated by the dashed lines for the {000ℓ} series of the diffraction spots, indicating a
Fig. 3. (a) TEM image of a double-side teethed ZnO nanocomb. (b) Diffraction pattern from the large circled area, showing the growth direction of the teeth is [0001]. (c) and (d) are convergent beam electron diffraction patterns from the upper tooth and the corresponding lower tooth of the nanocomb, as indicated by the small circles. The intensity distribution in the patterns indicates that both of the teeth are along [0001] direction but at 180° reversed polarity. (e) A magnified TEM image showing the existence of an inversion domain boundary parallel to the ribbon.

In the synthesis of the nanocomb structures, the teeth length of both single-sided and double-sided combs can be obtained from several hundred nanometers to tens of micrometers, depending on the temperature and pressure conditions for the experiments as well as the temperature zone where the substrates were placed in the furnace. In practice, nanocombs with longer teeth and the double-sided combs were acquired in a higher temperature zone.

Besides the two main comb structures reported above, other interesting comb-like structures were also found. The structure shown in Fig. 4a is the same type of asymmetric nanocomb as shown in Fig. 1, but it is directly linked to a tetraleg of ZnO [16], as indicated by an arrowhead. In Fig. 4b, the symmetric nanocomb has two-sided teeth, but the teeth are at an angle of ~110°. In Fig. 4c, a feather-like comb structure is shown, which has a similar structure as the one shown in Fig. 4b except the image was taken at an angle with the ribbon of the nanocomb that the angle between the two-sided teeth is not apparently shown.

The formation of the nanocombs in Fig. 4 can be explained from the octahedral multiply twinned nucleus that is responsible for the formation of the tetraleg [16], as shown in Fig. 5. The central octahedral nucleus is composed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra. A tetrahedron is a unit enclosed of eight tetrahedra.
nated (0001) planes, the growth of nanowires from the (0001) planes leads to the formation of the structures presented in Fig. 4b and c, with the teeth on both sides at an angle of $\sim 110^\circ$. Such structure was also found for ZnS [17].

In summary, single-sided and double-sided nanocomb structures were synthesized for ZnO. For the double-sided nanocomb, an inversion domain boundary is formed parallel to the {0001} plane along the growth direction of the central ribbon, so that the two sides of the ribbon are both terminated by the Zn-terminated (0001) surfaces. The Zn-(0001) polar surface defines the growth direction of the teeth out of the ribbon. Based on the multiply twinned octahedral nucleus of ZnO, the formation of the $\sim 110^\circ$ angular comb structure is also explained. Our data strongly support the active role played by the Zn-terminated (0001) plane in the growth of ZnO nanostructures.

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