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Using the mixture of zinc oxide and graphite powders as source materials, zinc oxide nanodisks with bulk quantity were fabricated by vapor-phase transport method. The nanodisks have perfect hexagonal shape with about 3 μm in diagonal and 300 nm in thickness. The growth is favored along six symmetric directions of $\pm[10\bar{1}0]$, $\pm[1\bar{1}00]$, and $\pm[01\bar{1}0]$ with the typical growth along [0001] direction suppressed, which directly leads to the formation of zinc oxide nanodisk. The microstructure and growth mechanism are discussed. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1811380]

Due to the unique electronic and optical properties, nanostructural materials have attracted great interests for their potential applications in electronics, photonics, chemical, and biochemical sensing. In the past decade, various nanostructures,[1–5] such as nanowires, nanotubes and nanoribbons, of metals, semiconductors and insulators have been fabricated by various approaches such as thermal deposition, chemical vapor deposition, and wet chemical method. Some one-dimensional nanomaterials such as carbon nanotubes[4] and InP nanowires[5] have been utilized successfully to nanodevices. The physical and chemical characteristics of the nanomaterials are strongly related to the nanostructure and orientation; therefore, it is very important to control the growth process further to obtain the desirable morphologies and crystal structures.

In recent years, great interests are focused on nanostructural zinc oxide (ZnO) because its wide direct band gap, strong excitonic binding energy and promising applications for UV-laser with low threshold,[6] field emission array,[7,8] surficial acoustic device,[9] transistor and biosensor[10] in nanoscale. Besides typical nanowire, nanorod, nanobelt, and nanotube, various fascinating nanostructures of ZnO, such as hierarchical and tetrapod nanowhisker, nanocomb, and nanopin, have been synthesized through different routes.[6–17] The reported fabrication methods mainly include vapor-phase transport (VPT),[11–14] metal organic vapor-phase epitaxy,[15] hydrothermal decomposition,[16] and electrochemical reaction.[17]

In contrary to one-dimensional nanostructures, disk-shaped morphology is less known, which has potential applications in information storage, transducer, light emitter, catalyst, and sensor. As reported, nanodisks of silver, cobalt, and gold, were generally produced in solution environment through wet chemical reaction, such as in colloidal state,[18] in polystyrenes template,[19] and in aqueous solution by laser ablation[20] or controlling selective adsorption of incoming elements by cetyltrimethylammonium bromide.[21] Sparse distributed nanodisks of metallic zinc were *in situ* formed in a high vacuum chamber of transmission electron microscope by electron-beam irradiation of single-crystal polyhedral Zn nanoparticles.[22] Recently, Tian *et al.*[23] synthesized ZnO nanoplates through a solution-based approach by using citrate anions to control the crystal morphology. Compared with all reported fabrication methods, VPT is the simplest and most effective approach to obtain nanostructures with bulk quantity, and it has been employed to fabricate all the earlier nanostructures of ZnO except nanodisks. In this letter, we will present high yield ZnO nanodisks with perfect hexagonal prism shape fabricated by the simple VPT method.

The fabrication of ZnO nanodisks was produced in a tube furnace similar to our previous works.[12–14] The source materials of the mixture of high purity ZnO and graphite powders were placed at the end of a slender one-end sealed quartz tube. A strip of silicon wafer with (100) orientation was used as substrate. The source temperature was kept at 1000 °C and the substrate temperature at about 600 °C. A white layer of product was deposited on the substrate after growth for 40 min. The scanning electron microscopy (SEM) was employed to examine the morphology of the product. The crystal structure of the sample was characterized by x-ray diffraction (XRD) using copper $K_{\alpha 1}$ radiation. The Raman scattering spectrum was measured by a Renishaw Ramanscope under the excitation of an argon laser operating at 514.5 nm. A JEOL 3010 high-resolution transmission electron microscope operated at 300 kV was employed to detect the lattice structure.

Figure 1 shows the SEM images with various magnifications. It is clearly seen that the substrate is covered with nanodisks, which indicates the high yield of nanodisks by VPT. It is noticeable that almost all nanodisks have perfect hexagonal shape with the uniform size of about 3 μm in diagonal and 300 nm in thickness. Although many nanodisks stack together, most of them lie on the substrate in horizontal

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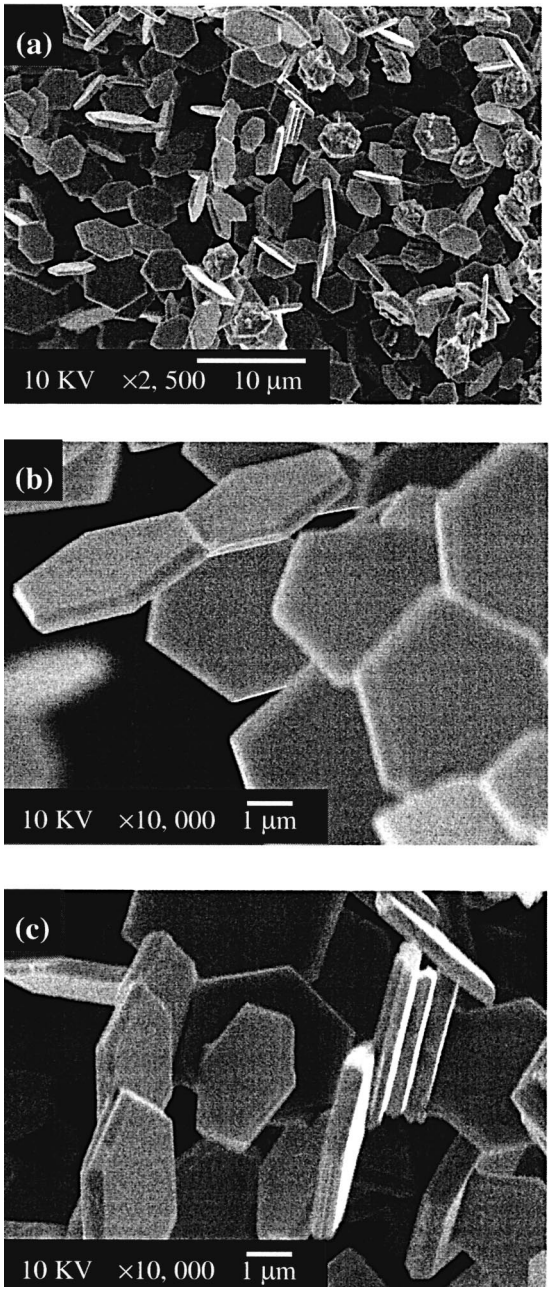

FIG. 1. SEM images of ZnO nanodisks with various magnifications: (a) dense nanodisks with bulk quantity, (b) enlarged nanodisks locating in horizontal position, and (c) some vertical standing nanodisks.

position [Fig. 1(b)] and some of them stand vertically [Fig. 1(c)].

The XRD pattern is illustrated in Fig. 2. As indexed in the figure, all diffraction peaks match with the wurtzite structural ZnO with lattice constants of $a=3.250$ Å and $c=5.207$ Å. The stronger diffraction peaks appear at 31.8°, 34.3°, and 36.5°, which correspond to $(10\bar{1}0)$, (0002), and $(10\bar{1}1)$ planes of wurtzite ZnO, respectively. Figure 3 shows the Raman scattering spectrum of the ZnO nanodisks. Besides the peak at 520 cm^{-1} originating from silicon substrate, a strong peak appears at 438 cm^{-1} which corresponds to the E_2 mode of wurtzite phase of ZnO.[24,25] The results of XRD and Raman spectrum confirm that the nanodisks are composed of hexagonal ZnO with good crystal quality.

Figure 4(a) is a high-resolution transmission electron microscopy (HRTEM) image of a nanodisk viewing from

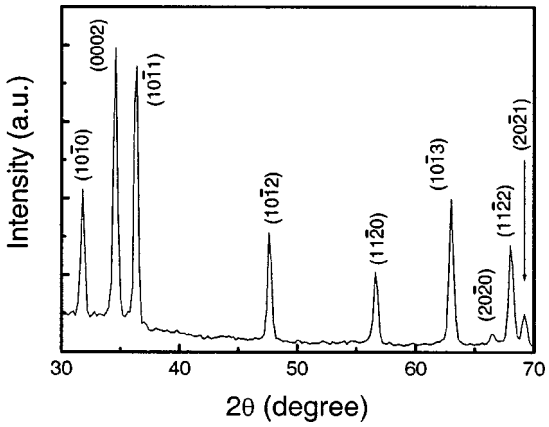

FIG. 2. XRD pattern of the ZnO nanodisks.

[0001] zone axis. It can be seen from HRTEM image that, the atoms arrange regularly to form a sixfold symmetric projected structure. Along these six symmetric directions indicated in Fig. 4(a), the d spacing is 0.28 nm, which corresponds to that of $(10\bar{1}0)$ planes. This indicates that the nanodisk grows mainly along the six symmetric directions of $\pm[10\bar{1}0]$, $\pm[1\bar{1}00]$, and $\pm[01\bar{1}0]$, and the growth along [0001] is suppressed, as illustrated in Fig. 4.

The growth mechanism of the nanodisk is not clear yet. In general, the polar crystal of ZnO nanostructures grows preferentially along [0001] direction (+c axis terminated by zinc) because of the lowest surface energy of (0002) facet. The growth velocity along $\langle 10\bar{1}0\rangle$ directions is slower than that along [0001] direction;[26,27] therefore, the nanowire morphology is often obtained. The nanodisk can be produced by suppressing the growth along +c axis in certain conditions. Based on this idea, ZnO nanoplates have been synthesized in solution using citrate anions as structure-directing agent to adsorb selectively on ZnO basal planes.[23] In the present case, the suppression effect is likely originated from Zn liquid droplets in a self-catalyst vapor-liquid-solid process that is similar to the formation of SnO nanodisks fabricated by thermal evaporation.[28] The Zn vapor is generated by thermal carbon reduction of ZnO in the source region at high temperature. The metallic Zn vapor transfers to the low temperature region and condenses into liquid droplets, and then oxidized into ZnO nucleus with hexagonal facets. Similar to this process, *in situ* formation of metallic Zn nanodisks[22] have

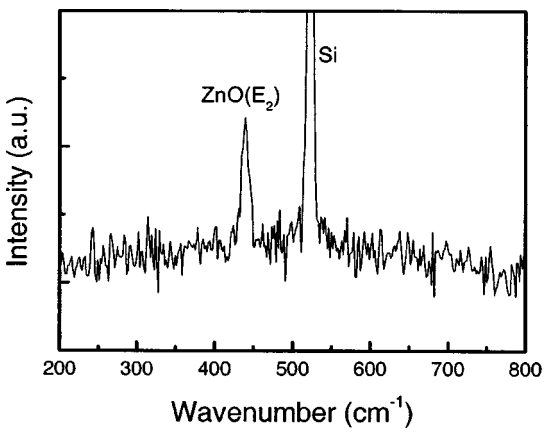

FIG. 3. Raman scattering spectrum of the ZnO nanodisks.

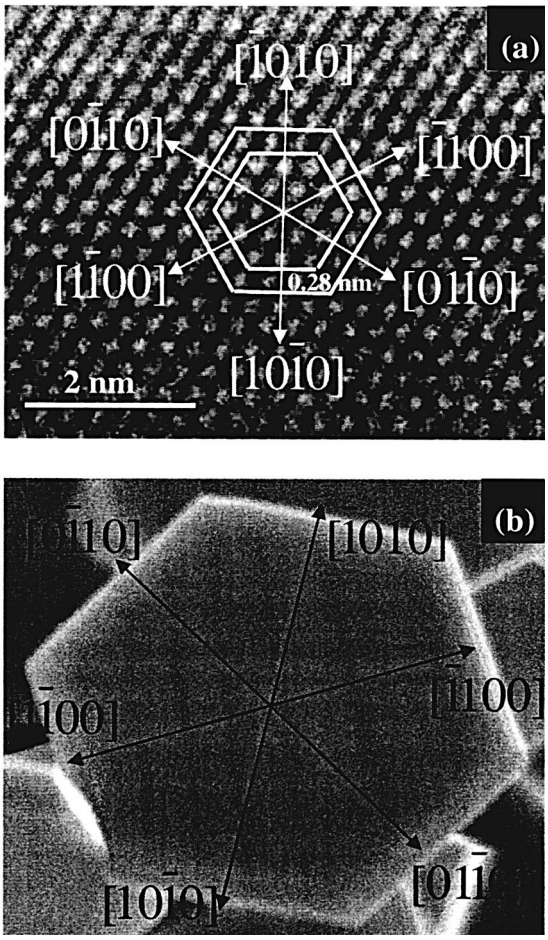

FIG. 4. (a) HRTEM image of a nanodisk with six-fold symmetry. The crystal orientations and the d-spacing are indicated. (b) The corresponding SEM image with crystal orientations indicated.

been observed in TEM chamber with high vacuum by electron beam irradiation of polyhedral Zn powders. For the hexagonal structural Zn and ZnO crystals, the top surface is (0002) plane and the side surfaces are $\{10\bar{1}0\}$ planes with low surface energy. If the (0002) facet of the crystallized ZnO are constantly kept clean and the newly incoming droplets can constantly wet and cover the entire condensed (0002) facet, the ZnO nanodisks with geometrical shape of hexagonal projections can be obtained.[2] In our experimental conditions, the mobility of the Zn atoms in vapor was high enough to form flat (0002) surfaces which prevented the accumulation of incoming atoms or molecules.[29] The smooth surface of the nanodisk, as shown in the SEM image in Fig. 4(b), provides the evidence for this assumption. The growth temperature was much higher than the melting point of metallic Zn (419 °C), therefore, it was high enough to keep the liquid state of the newly arriving droplets during the growth of ZnO nanocrystals. Due to suppression of growth on (0002) facet with the lowest energy, the crystals would grow mainly along the six directions of $\langle 10\bar{1}0\rangle$, which have the second lowest surface energy. The same growth velocity along these six directions leads to the formation of the six-fold symmetric nanodisks with hexagonal shape.

In summary, high yield nanodisks with perfect hexagonal shape have been fabricated by the VPT method. The analysis of the microstructure demonstrates that the large smooth surface of the nanodisks is (0002) plane and the six symmetric side surfaces are $\pm(10\bar{1}0)$, $\pm(1\bar{1}00)$, and $\pm(01\bar{1}0)$. The growth suppression along $+c$ axis is probably due to wet droplets of Zn under proper temperature and vapor pressure.

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