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Temperature-dependent growth mode and photoluminescence properties of ZnO nanostructures

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Abstract

ZnO nanostructures have been synthesized using a catalyst-assisted carbothermal reduction approach on Si substrate. By analyzing SEM images, two different growth mechanisms were found to grow ZnO nanostructures. At low growth temperature (900 and 950 °C), vapor–solid mode is dominant in the growth process. With increasing the growth temperature to 1000 °C, ZnO nanorods grow followed vapor–liquid–solid process. The role of catalyst in these two growth processes is discussed. In room-temperature photoluminescence measurement a strong excitonic emission located at 3.25 eV was observed for ZnO obtained at the growth temperature of 1000 °C.

Zinc oxide, which has a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, has attracted much interest for a wide range of applications such as ultraviolet/blue emission device, solar cells, piezoelectric devices, acousto-optical devices and chemical sensors [1–3]. Recently some low dimensional ZnO nanostructures, including nanorod [4], nanobelt [5], nanotube [6], and nanosheet [7], have been reported due to their potential application in constructing nanoscale electronic and optoelectronic devices. Heterostructural nanowires have already been employed in lasers [6], sensors [8], nanoresonators and cantilevers [9], and field-emission devices [10].

Various techniques have been used to prepare ZnO nanowhishers, such as arc discharge, laser vaporization, pyrolysis, electrodeposition, physical vapor deposition, chemical vapor deposition (CVD), and soft chemical method [11–13]. In syntheses of aligned one dimensional (1D) ZnO nanostructures, catalysts such as Au [3], Co [11], and NiO [14] have been introduced into the synthesis process to orient ZnO nanowires growth, and aligned growth without catalysis has also been achieved using low-temperature CVD [12], metal-organic chemical vapor deposition (MOCVD) [10]. The ZnO nanorods growth is described by vapor–liquid–solid (VLS) and vapor–solid (VS) mechanisms [3–5,15–17]. But the detailed understanding of the low dimensional ZnO nanostructure growth mechanism is still incomplete. For example, when using a metal catalyst in the growth process some articles reported that an alloy droplet was found on the tip of nanorod, but others showed nothing could be observed on the tip. In this Letter, ZnO nanorods and nanosheets are obtained on Si substrate by controlling growth temperature. The probable nucleation and growth mechanisms of ZnO nanostructure are discussed.

The ZnO nanostructures were fabricated via a simple vapor-phase transport process in a conventional furnace

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with a horizontal quartz tube (the inner diameter of quartz tube is 4 cm). A mixture of commercial ZnO and graphite powders in a certain weight ratio (1:1) was placed in an alumina boat as the source material. The polished side of Si (100) wafer is covered with Au coating obtained by sputtering served as catalyst. This coating is composed of nanosized islands, and is around 6 nm equivalent thickness. The Au coated side was faced downward on the alumina boat with a separation of about 5 mm. At same time a bare Si substrate was also put side by side on the alumina boat. Synthesis was carried out at different temperature from 900 to 1000 °C under a constant flow of Ar (99.99% purity) of 50 sccm for 30 min (a thermal couple was put close the substrate). After the reaction, a light gray layer was only found on the Au coated substrate surface, nothing was observed on bare Si substrate. Morphological and crystallographic properties of the as-grown samples were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), selected-area electron diffraction (SAED) and energy dispersive X-ray analysis (EDX) (the diameter of electron beam in SAED and EDX is less than 100 nm). The photoluminescence spectra were obtained with a He–Cd laser of 325 nm wavelength at room temperature.

Fig. 1 shows typical FESEM images of as-prepared samples grown at different temperatures from 900 to 1000 °C. The diameters of ZnO nanorods grown at 900 °C normally range from 50 to 100 nm and their lengths are 5–10 μm (Fig. 1a). Some branches with the same size are also observed (Fig. 1b). With increasing the growth temperature to 950 °C the branches disappear, the diameters of ZnO nanorods increase to 60–140 nm, and the lengths decrease to 1–3 μm (Fig. 1c and d). The hexagonal-shaped cross-section of ZnO nanorod is clearly seen from the top view of the amplified SEM image (shown in the insert of Fig. 1d). In

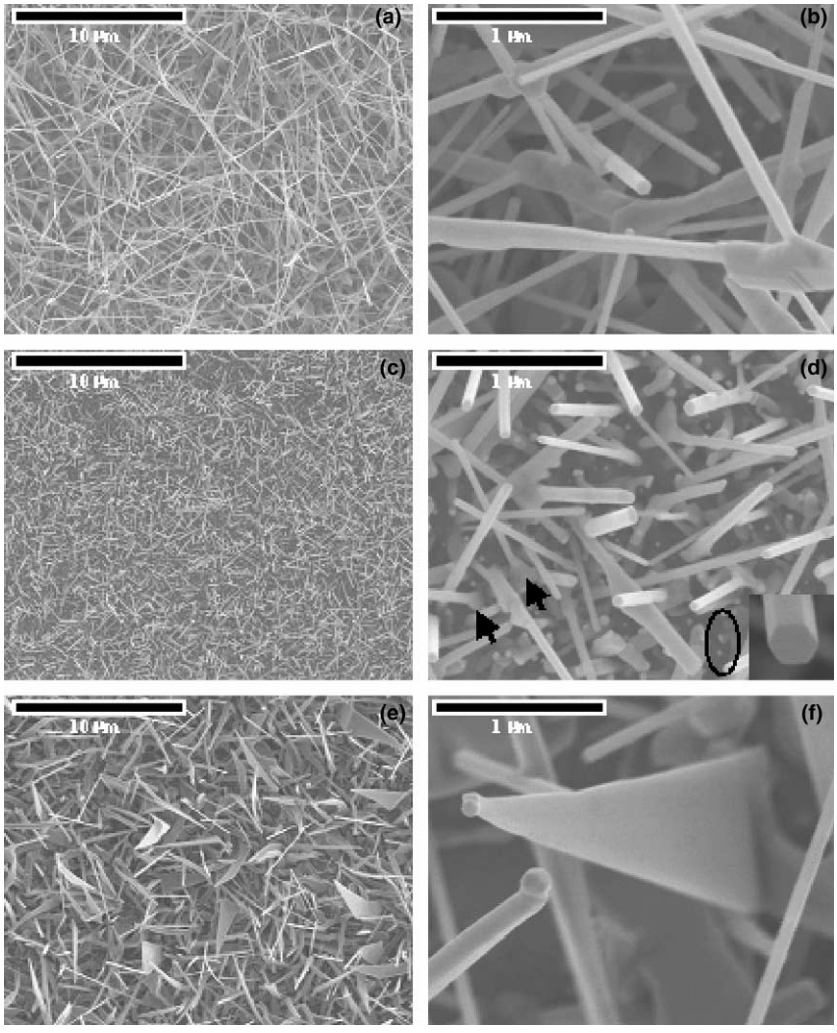

Fig. 1. FESEM images of ZnO nanorods grown on Au coated Si substrate at 900 °C (a,b), 950 °C (c,d), and 1000 °C (e,f), respectively. The insert of Fig. 1d shows the hexagonal-shaped cross-section of ZnO nanorod. The black ring shows some nanoclusters, and the black arrows indicate the large roots of nanorods.

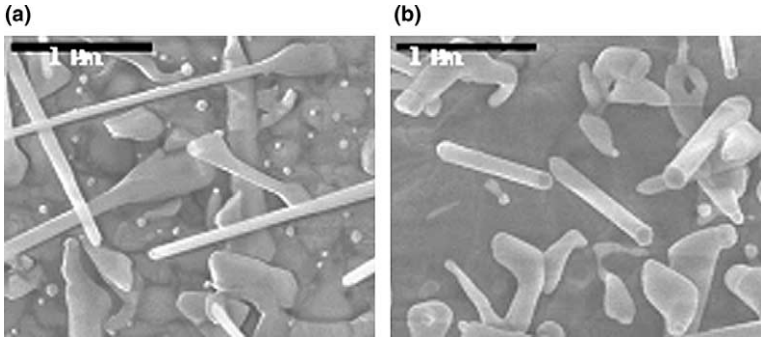

Fig. 2. FESEM images of ZnO nanorods grown at 950 °C (a) and 1000 °C (b) with an Au thin film of 3 nm equivalent thickness.

Fig. 1d we can see some nanoclusters (enclosed by a black ring in Fig. 1d) with the diameter of 20–50 nm just on the substrate, which is much smaller than the diameter of nanorods. Energy dispersive X-ray analysis shows these nanoclusters are composed of Au, Zn, and O. As indicated by black arrows in Fig. 1d the roots of nanorods are larger than the nanorods size.

At growth temperature of 1000 °C, in addition to nanorods (diameter increasing to 100–200 nm) some non-regular shaped ZnO nano-sheets are present on the substrate (Fig. 1e and f). The thickness of ZnO nano-sheet is as the same order as nanorods (around 100 nm). A droplet could be found on the tip of each ZnO nano-rod and nano-sheet (we have observed different parts on the sample, the images of each part like Fig. 1f). While for nanorods grown at 900 and 950 °C no droplet was detected on the tip.

In order to observe the whole nanorods clearly, we grew ZnO nanorods at 950 and 1000 °C with less Au catalyst (the equivalent thickness of Au thin film decreased to 3 nm). The FESEM images in Fig. 2a show each nanorod grows on a larger root. EDX analysis indicates the ZnO nanorods roots contain Au, Zn and oxygen, which means an alloy (Au/Zn) nanocluster is coexisted with ZnO. Different to Fig. 2a, nanorods grown at 1000 °C is homogeneous diameter with a droplet on the tip (Fig. 2b). EDX analysis made on the droplet indicates that it is mainly gold with only less than 1 at.% of Zn. Considered the precision of EDX analysis it is difficult to conclude if the droplet is only gold or if the droplet contained very small amount of zinc (less than 1 at.%).

Fig. 3a shows the TEM images of ZnO nanorods obtained at 950 °C. In this case no droplet is observed at the nanorod tip. Electron diffraction pattern and high resolution TEM image given in the insert indicate that the nanorod is a single crystal, which shows the nanorod is hexagonal (wurtzite) structured ZnO with lattice parameters of $a = 0.32$ nm and $c = 0.52$ nm. The nanorod grows along [0 0 0 1] direction as indicated by HR-TEM (lattice spacing of 0.26 nm). TEM imaging of a ZnO nanosheet with a droplet grown at 1000 °C is pre-

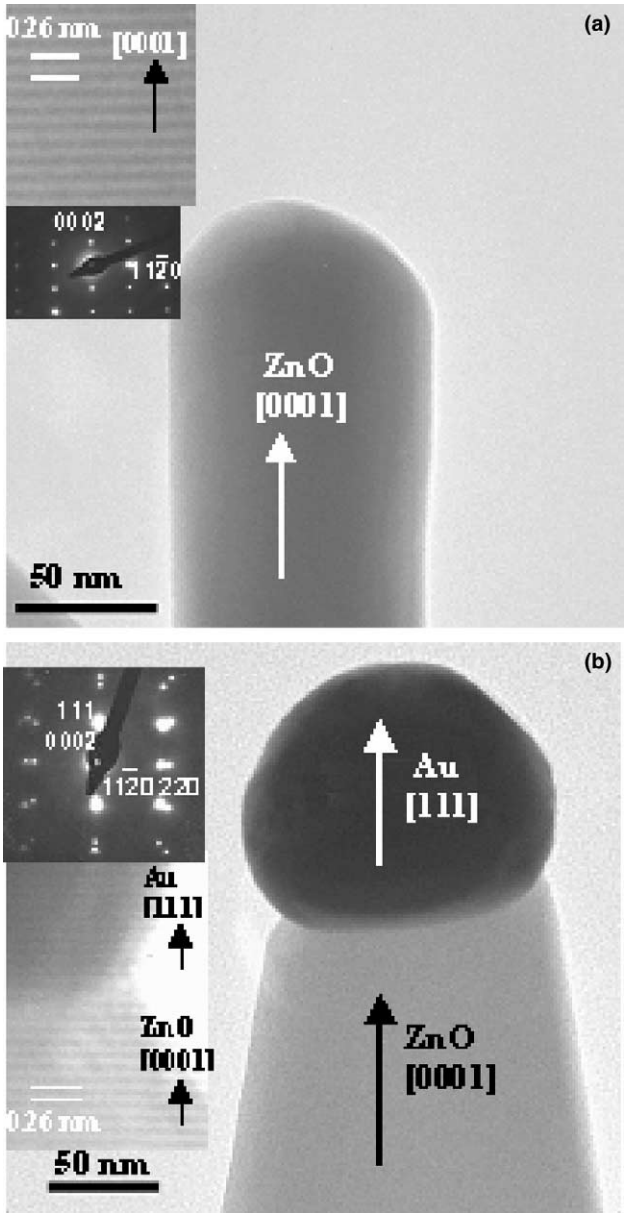

Fig. 3. TEM images of a single crystalline ZnO nanorod grown at 950 °C (a) and a nanosheet (grown at 1000 °C), (b) with a droplet on the top. The insets in a and b show the corresponding selected-area electron diffraction patterns and HR-TEM images.

sented in Fig. 3b. The nanosheet is single crystalline with the main growth direction along c axis. The SAED shows that there is a coherent relation between the ZnO lattice and the droplet lattice. The droplet lattice is the cubic gold lattice with $a = 0.41$ nm. In this case the [0 0 0 1] nanosheet direction is parallel to the [1 1 1] gold direction and the interface between the droplet and ZnO is atomically sharp.

Two processes have been suggested for the growth of ZnO nanorods. One is the oxidation of the reduced and vaporized Zn following the VLS growth process, and the other is VS process. The essential of VLS mechanism is the liquid phase, which could guide the growth direction. Usually when using catalyst growth method, the source material could dissolve into catalyst to form a liquid phase. When this phase is supersaturated nanorods grow. This mechanism agrees well with our samples grown at 1000 °C, because an alloy droplet was observed on the tip. But when we use this mode to explain the samples grown at 900 and 950 °C, there are some problems. Where is the liquid phase, on the tip or at the root? And what is the role of catalyst in this process?

In order to describe the growth process detailedly, three steps are assumed for growing ZnO nanostructure, including alloying, nucleation and growth, referring to the growth mechanism of other semiconductor nanowires [18]. This process could be affected by the concentrations of Zn atoms and oxygen source (CO/H_2O), and the substrate temperature. In our case the Zn and CO vapors are only generated by the reaction between ZnO and graphite. The concentrations of Zn vapor and oxygen source (CO/H_2O) could be controlled at low values. Because the growth temperature is higher than 900 °C, the Zn adatoms can just stay on the substrate for a very short time. If there is no special nucleation site on the substrate Zn atoms will re-evaporate from substrate without being oxidized (the boil point of Zn is 907 °C). Therefore, no product could be found on bare Si substrate.

When Au is used as catalyst, Zn atoms can be dissolved in Au nanoclusters with forming a Zn/Au alloy. By analyzing the Zn/Au alloy phase diagram, the alloy could be present with wide atom ratio of Zn and Au, when the temperature is beyond 900 °C [19]. The Zn atoms contained in the alloy are oxidized to form a nucleation site for ZnO nanorods growth. Because at 900 and 950 °C the concentration of zinc vapor is relatively low, only small amount of Zn atoms could diffuse into Au nanoclusters with forming a solid solution. The adsorbed Zn atoms could react with CO/H_2O to form the nucleation sites, which is mainly covered the droplet surface leading to the formation of a large ZnO shell. At the growth temperature of 950 °C, Zn and Zn suboxides (the melt points of Zn and ZnO_x is approximately at 419 °C, $x < 1$) should be in vapor phase. No liquid phase is present in the growth process. Therefore, the growth of ZnO single crystal rods follows a VS process. The tip of ZnO rod is hexagonal-shaped without any alloy droplet on the top, and the root of nanorods is larger (Fig. 1d and Fig. 2).

When increasing the growth temperature to 1000 °C, the Zn/Au alloy formed with high concentration of Zn becomes liquid state. As the droplets become supersaturated, crystalline ZnO nanostructures are formed by the reaction between Zn and CO/H_2O vapor. The interface between alloy droplets and substrate (or ZnO rods) plays an important role in the nucleation and growth process of ZnO nanorods. ZnO nanostructures grow following three steps: liquid alloy, oxidization, and ZnO growth. So the VLS mechanism is dominant in the growth process of ZnO nanostructure along [0 0 0 1] direction. Beside the growth of [0 0 0 1] direction, the excess Zn atoms without being dissolved by Au cluster could also be bonded to the side face of ZnO nanostructure (1 1 2 0), which leads to 2D growth mode present. This is a catalyst-free growth process. ZnO nanosheets with an alloy droplet on the tip could be obtained (Fig. 3b).

Fig. 4 illustrates the room-temperature photoluminescence spectra of ZnO nanostructures grown at different temperatures. An ultraviolet emission located at 3.25 eV is observed for all the samples, which originates from the radiative recombination of exciton. Differing from other reports, an emission band at 3.0 eV is detected for the samples grown at low temperature (900 and 950 °C). With increasing the growth temperature the intensity of this band decreases and finally disappears at 1000 °C. This 3.0 eV emission band is attributed to the recombination of an electron with a deeply trapped hole in the V_{Zn}^{-} center, which means the concentration of Zn vapor is lower than oxygen source at 900 °C in ambient atmosphere [20]. When increasing temperature the

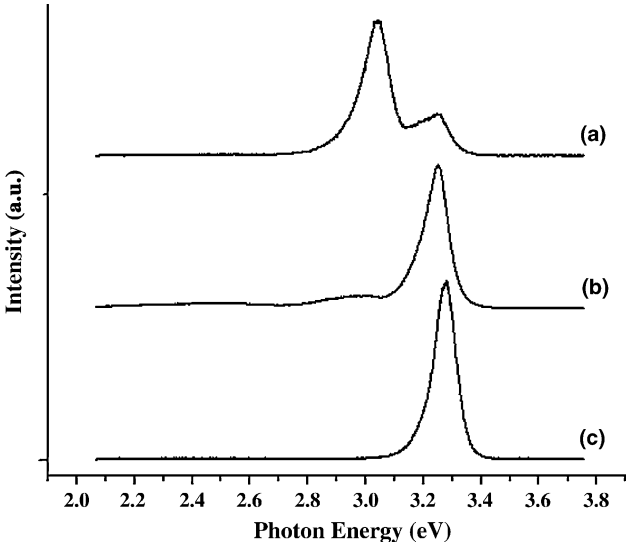

Fig. 4. Photoluminescence spectra of ZnO nanostructures grown at different substrate temperatures ((a) 900 °C; (b) 950 °C; (c) 1000 °C).

concentration of Zn vapor increases and the growth of ZnO nanostructure tends to stoichiometric.

In conclusion, ZnO nanorods could be fabricated following different mechanism: VLS or VS. The presence of Au catalyst is mainly used to fix the Zn atoms with forming a Zn/Au alloy. At a certain growth temperature, when the alloy is liquid the growth process is VLS. Otherwise, when this alloy is only a solid solution nanorods grow following VS mechanism.

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