NANO PERSPECTIVES

The Periodic Instability of Diameter of ZnO Nanowires via a Self-oscillatory Mechanism

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Abstract ZnO nanowires with a periodic instability of diameter were successfully prepared by a thermal physical vapor deposition method. The morphology of ZnO nanowires was investigated by SEM. SEM shows ZnO possess periodic bead-like structure. The instability only appears when the diameter of ZnO nanowires is small. The kinetics and mechanism of Instability was discussed at length. The appearance of the instability is due to negative feed-back mechanism under certain experimental conditions (crystallization temperature, vapor supersaturation, etc).

Introduction

Various unusual morphologies of whiskers and nanowires have been reported in past few years [1–9]. Since its discovery by Wagner and Ellis in [10], the vapor–liquid–solid (VLS) growth mechanism [10] has been used to explain the formation of the majority of vapor grown whiskers and nanowires. The typical morphology of whiskers and nanowires is that each whisker or nanowire terminates with a catalyst particle on its end. Sears also propose another growth model, so-called vapor–solid (VS) mechanism [11], to explain the initialization of the one-dimensional growth of nanowire or whisker with a catalyst-free process as followings: if the supersaturation is below the value required for the formation of a crystal of some material with euhedral morphology, anisotropic one-dimensional growth occurs in specific crystal directions. The nanowires or whiskers grown via VS mechanism usually terminate with a sharp tip. Moreover, a screw dislocation growth model (SD) [12] is also proposed by Sear to explain the formation of some whiskers under substrate stress. Usually, there is a dark-line at the axial center within the whisker under TEM analysis.

Recent years a new kind interesting structure, periodic bead-like structure, has been discovered. Dai et al reported that Ga_2O_3 chains with closely spaced knots connected by nanowires were acquired by thermal evaporation method [13]. Wang et al successfully synthesized Zn_2SnO_4 nanowire with periodic structure by the thermal evaporation method [14]. Chains of crystalline-silicon nanospheres were formed by a self-organized process via an extension of the vapor-liquid-solid mechanism using gold as catalyst by Kohno et al. [15, 16]. In addition, Xie's group successfully prepared In_2O_3/SnO_2 Hetero-junction beaded nanowires via a simple thermal vapor deposition method [17]. Liu et al prepared periodically structured single-crystalline zinc branches by electrodeposition method [18].

Here, we report another interesting growth model for formation of a novel structure (periodic instability of diameter) of ZnO nanowires via catalyst free vapor deposition method. To our knowledge, it's the first time to report the structure of periodic instability in ZnO nanowire. The formation of this kind of structure can be explained by self-oscillatory mechanism.

Experimental

The preparation of the ZnO nanowires was performed in a conventional furnace with a horizontal alumina tube. In a

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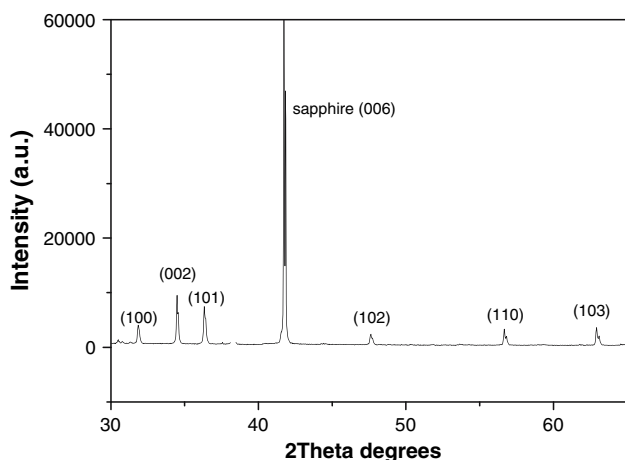e-mail: yezhang@issp.ac.cn

Fig. 1 XRD spectrum of ZnO nanowires on sapphire

typical process, the sapphire substrate was put onto an alumina boat loaded with a mixture of Zn (purity: 99.999%), carbon and ZnO powders. The alumina boat was then transferred into the center of the tube furnace. Then, the chamber was heated up to 950 °C at a rate of 20 °C/min under a 200 sccm constant flow Ar (2%O_2 in Ar) and kept for 20 min. After cooling down, a white layer was found deposited on the sapphire substrate. The as-prepared products were characterized by field emission scanning electron microcopy (SEM) (SEM: Sirion 200 FEG), X-ray diffraction spectra (XRD) (Philips X'pert-PRO, Cu Kα (0.15419 nm) radiation) and X-ray photoelectronic spectroscopy (XPS).

Results and Discussion

X-ray diffraction pattern (Fig. 1) shows that all diffraction peaks can be indexed to those of the hexagonal wurtzite phase of ZnO and sapphire substrate. No other phases were detected. Low-magnification SEM (Fig. 2a) demonstrates that a large number of nanowire were randomly deposited on sapphire substrate. The average length of ZnO nanowire is 5 μm and the diameters of nanowire range from 100 nm to 200 nm. EDX and XPS (Fig. 3) analysis also shows that the nanowires consist of Zn and O elements. High resolution SEM image (Fig. 2b) indicates that each nanowire possess bead-like periodic structure. The diameter of nanowire change periodically and the distance between knots is uniform. It could be seen that periodic structure only appears when the diameter of wire is small. For nanowires with large diameter, the periodic instability diminishes (Fig. 2c).

The occurrence of periodic instability of diameter of nanowires is induced by self-oscillatory mechanism. In the initiative stage, a Zn rich droplet was formed on the substrate and then Zn, O species is absorbed in the droplet. Continuous dissolving Zn and O species into the droplet lead to the saturation and one-dimensional crystal growth of ZnO. This

Fig. 2 SEM images of periodic bead-like ZnO nanowires on sapphire: (**a**) low-magnification image of periodic bead-like nanowire; (**b**) low-magnification image of periodic bead-like nanowire; it could be seen the periodic instability diminishes when diameter is large; (**c**) high low-magnification image of periodic bead-like nanowire
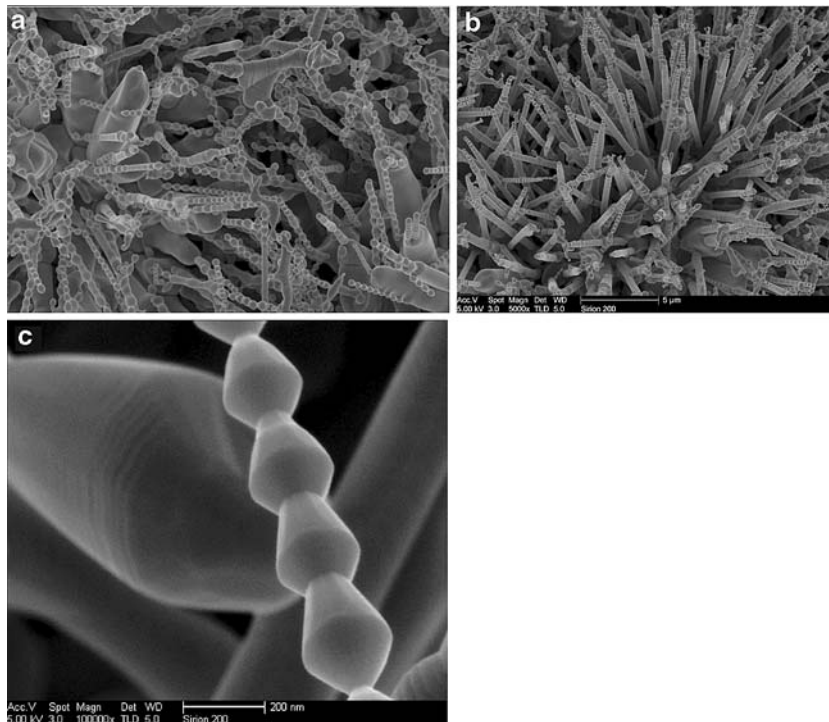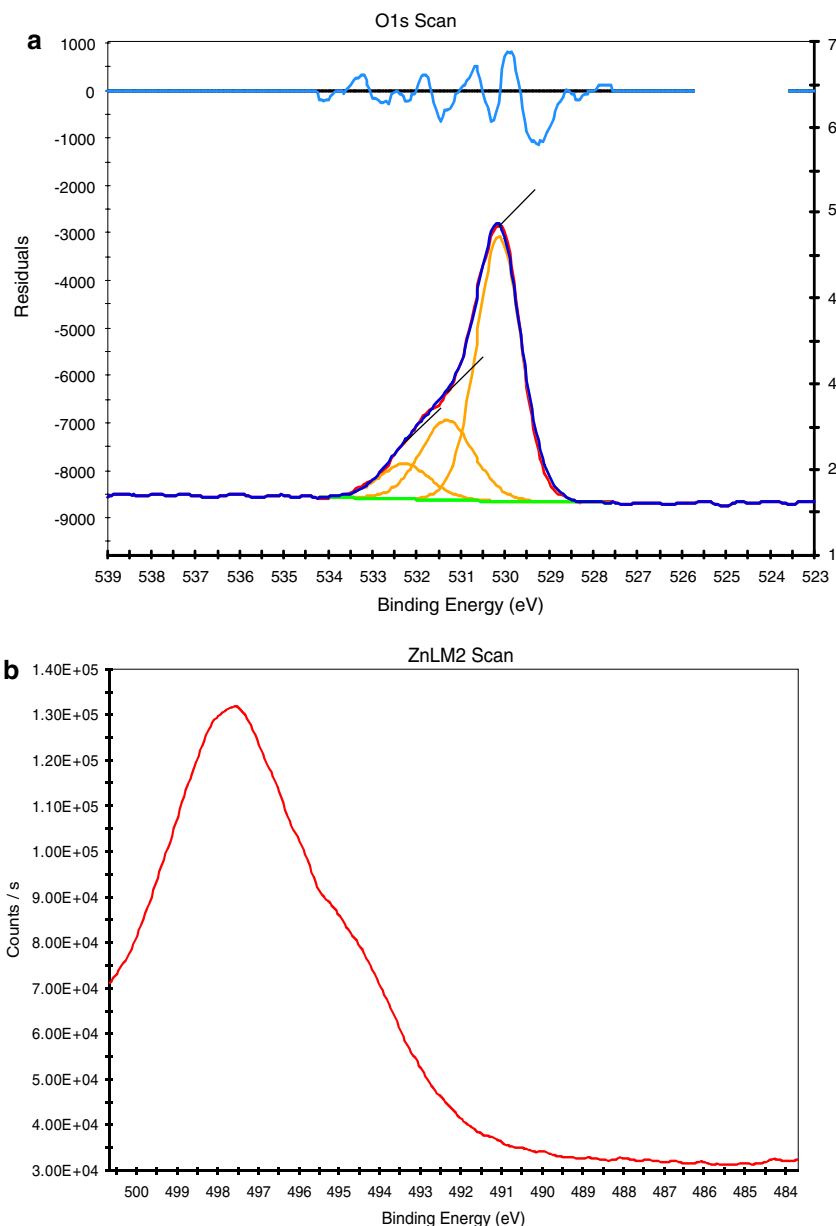
Fig. 3 XPS spectrum of ZnO nanowires. (**a**) O element, (**b**) Zn element

process is similar to VLS process, in which Zn droplet play as a self-catalyst nucleation site for nanowire growth. During growth of nanowires, the oscillation of diameter of wire occurred under certain conditions (crystallization temperature, vapor supersaturation, etc.) within the range, within of which the Gibbs-Thomson effect works. The feedback could be described with a feedback model [19] as followings:

1. Positive feedback: if the diameter of nanowire decrease, the concentration of O in droplet will increase due to the lowering of consumption of O at the liquid–solid interface, then the roughness of the liquid–solid interface increases, and hence the diameter of nanowire decreases further.

2. Negative feedback: If the diameter of nanowire decreases, the mole fraction of O in the droplet decreases because the curvature of the Zn droplet increases (the Gibbs–Thomson effect); Then, the roughness at solid-liquid interface (the liquid phase is O in Zn droplet; solid phase is ZnO) decreases, and the diameter increases, and so on, and then an oscillation of wire diameter occurred.

Positive feedback will lead to the continuous expanding or shrinking of nanowire. When negative feedback dominated, oscillation occurs.

When negative feedback dominates (the Gibbs–Thomson effect be ineffect), the relation of diameter of nanowire

and concentration of O in droplet can also be explained by following equations [20]:

$$\frac{dc}{dt} = \eta(x - x_0) \tag{1}$$

$$\frac{dx}{dt} = -\kappa(c - c_0) \tag{2}$$

where x_0 denotes the mean diameter, c denotes the concentration of O in droplet. η and κ denote the positive coefficient, and t denotes the time.

From the above Eqs. 1 and 2, we have Eq. 3

$$\frac{d^2x}{dt^2} = -\kappa\eta(x - x_0) \tag{3}$$

This equation is a harmonic oscillator resolution. It means that the periodic structure of nanowire develop through a self-oscillation mechanism.

The reason why the periodic instability vanish at large diameter could be understood as followings:

The O supersaturation (vapor phase/liquid phase) of $\Delta\mu/kT$ can be determined by following equation [21]:

$$\frac{\Delta\mu}{kT} = \left(\Delta\mu_0 - \frac{4\Omega\gamma}{d}\right)/kT \tag{4}$$

$\Delta\mu$ denotes the difference between the chemical potentials of O in vapor phase and in droplet. $\Delta\mu_0$ denotes the same difference at a plane interface ($d\to\infty$), Ω denotes the atomic volume of O. From this equation, we know that diameter of droplet increase and the supersaturation will increase and approach to the value of $\Delta\mu_0/kT$. In a word, the larger the diameter of nanowire is, the larger the diameter of Zn droplet is, and the higher supersaturation of the liquid–solid interface is. As the supersaturation increase (diameter: 200–500 nm for ZnO), the epitaxial growth will manifest itself by masking the periodic structure; hence the periodic structure will disappear. In addition, the Gibbs–Thomson effect also could not bring into play at high supersaturation.

Conclusions

In summary, ZnO nanowires, with periodic bead-like structure, were prepared by thermal physical vapor deposition method. A self-oscillation mechanism was employed to explain the formation of such unusual morphology. This mechanism only manifests itself when the diameter of nanowire is small (<200 nm). These nanostructures are expected to be useful in optoelectronics and provide much useful information for researcher to understand the growth mechanism of nanowire or whisker.

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