Growth Mechanism of Needle-shaped ZnO Nanostructures over NiO-coated Si Substrates

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Abstract—ZnO nanostructures were synthesized over NiO-coated Si substrate by a thermal evaporation of Zn powders in a vertical chemical vapor deposition reactor. The ZnO nanostructures had a needle-like morphology and the diameter of the structures decreased linearly from the bottom to the top. The bottom diameters of the ZnO nano-needles normally ranged from 20-100 nm and the lengths were in the range of 2-3 µm. The clear lattice fringes in HRTEM image indicated the growth of good quality hexagonal single-crystal ZnO. Field emission characteristics of the ZnO nano-needles showed that the turn-on field was about 8.87 V/µm with a field enhancement factor of about 1099. The growth mechanism of the ZnO nano-needles was proposed on the basis of experimental data.

Key words: ZnO Nanostructures, Nano-needles, Evaporation of Zn, Characterization, Growth Mechanism

INTRODUCTION

Nanoscale one-dimensional materials such as nanotubes and nanowires have been successfully synthesized and have received much attention due to their extraordinary physical properties and potential application for nanodevices [Yang et al., 2002; Nahm et al., 2003; Park et al., 2002]. Owing to exceptional physical properties of ZnO such as high conductance, chemical and thermal stability, wide band-gap, and high piezoelectric coupling coefficient, it has been studied for piezoelectric devices and short wavelength (green/green blue) electro-optical devices [Zheng et al., 2002; Wang et al., 2002]. Electron field emitters in field-emission flat panel displays (FED) are another potential application area of semiconductor nanowires or nanotubes [Zhu et al., 1999; Lee et al., 2002]. Some wide band-gap semiconductors were reported as good electron field emitters because they have a high mechanical strength, and chemical stability [Frederick et al., 1999; Chen et al., 2001; Wu et al., 2002; Liu et al., 2002; Sohn et al., 2000; Kim et al., 2001]. The synthesis of one-dimensional ZnO material has been carried out using various methods such as arc-discharge [Choi et al., 2000], laser vaporization [Wu et al., 2002], template-based methods [Zhu and Fan, 1999; Li et al., 2000], high temperature physical evaporation [Wang et al., 2002] and reduction and oxidation of ZnS [Hu et al., 2002]. Most of the previous works have reported the growth of ZnO nanowires and nanobelts. Recently, relatively few papers [Park et al., 2002; Lee et al., 2003; Zhu et al., 2003; Tseng et al., 2003] have reported the growth of needle-like ZnO nanostructures, and the growth mechanism of the ZnO nano-needles has not been fully understood in the works.

In this work, we report the synthesis of needle-shaped ZnO nanostructures over NiO-coated Si substrate in a vertical chemical vapor deposition (CVD) reactor. The ZnO nanostructures were grown by thermal evaporation process of Zn powders under N2 flow. The structural and electrical properties of the grown needle-like ZnO nanostructures were investigated by using various analytic techniques. The growth mechanism of the ZnO nano-needles was proposed on the basis of experimental results.

EXPERIMENTAL

ZnO nanostructures were synthesized by using a vertical CVD reactor depicted in Fig. 1 [Ahn et al., 2002]. The surface of Si (100) substrate (1.5 cm×6 cm) was first scratched with a fine sand paper to hold NiO well on the substrate and was then sonicated in acetone. A solution of 0.01 M Ni(NO3)2·6H2O dissolved in ethanol was dropped on the cleaned Si surface. Then Ni(NO3)2-coated Si substrate was dried in an oven for 24 hr. Metal Zn powders (2 g) were loaded in an inner reactor and then the Ni(NO3)2-coated Si substrate was vertically set up over the Zn source. The inner reactor was placed...
in an outer quartz reactor. Nitrogen gas was introduced into the outer reactor through a delivery tube and the temperature of the furnace was heated to 500 °C under 20 scm N₂ (99.99%) gas flow. It was reported that Ni(NO₃)₂ readily decomposes at ~260 °C to be NiO [Llewellyn et al., 1997]. The growth of ZnO nanostructures was carried out at 500 °C under N₂ gas flow. After the growth reaction, light ash-colored materials were found on the surface of the substrate and the materials were uniformly deposited at 2-4 cm distance between Zn source and substrate. The flow of N₂ gas was maintained during the reaction and the reactor was cooled to room temperature under the N₂ flow.

RESULTS AND DISCUSSION

ZnO nanostructures were grown for 60 min at 500 °C under N₂ gas flow at different reaction times. Light ash-colored materials were deposited on Si surface and were characterized by using XRD measurements. Fig. 2 shows an XRD pattern of the deposited materials on NiO coated Si substrate. The spectrum is almost equal to the typical XRD spectrum of ZnO reported in the previous papers [Lee et al., 2003; Sun et al., 2002]. The spectrum shows peaks at 2θ = 31.2, 33.88, 35.64, 47, 56.04, and 62.48 for ZnO (1010), ZnO (0002), ZnO (1011), ZnO (1012), ZnO (1120), and ZnO (1013), respectively. The diffraction peaks are indexed to be a wurtzite structure of ZnO and the strong intensities of the peaks present the growth of ZnO crystalline. It is not found that there are any other peaks due to the presence of unreacted Zn and other impurities except for Si substrate peak at 2θ =33.1, 61.2, 69.132 for Si (002), Si (004) Kβ, and Si (004), respectively [Kim et al., 2001; Boo et al., 2000]. All the samples prepared in this experiment showed the similar XRD patterns, indicating the growth of ZnO crystalline. The ZnO nanostructure lattice constants calculated from the XRD data by using the Rietveld refinement method were a=3.241 and c=5.190 Å, consistent with those of bulk ZnO (JCPDS 75-0576).

Shown in Fig. 3 is an FE-SEM image for ZnO nanostructures grown on silicon substrate. The image presents the growth of vertically aligned ZnO nanostructures with high regularity and density. It is interesting to note that the diameter of the nanostructures decreases with increasing the length of the nanostructures from the bottom to the top to form a needle-shaped structure. The tip of the ZnO nano-needles is well developed without the formation of metal or metal oxide tips. EDX analysis also identified the absence of Ni or NiO on the sharpened tips. This result proposes that the nano-needles grow upward from the substrate surface. The diameter of the nano-needles normally ranges from 20-100 nm and the lengths are 3-5 µm long, though the diameter decreases as they grow.

Fig. 4(a) is a TEM image for the grown ZnO nano-needles. The

Fig. 2. A typical X-ray diffraction pattern of ZnO nano-needles grown at 500 °C for 60 min under N₂ gas flow.

Fig. 3. A typical SEM image of ZnO nano-needles grown at 500 °C for 60 min under N₂ gas flow.

Fig. 4. TEM and HRTEM images of ZnO nano-needles grown at 500 °C for 60 min under N₂ gas flow.