Possibility of Shape Control of ZnO Nanostructures Grown by Atmospheric-pressure CVD Utilizing Catalytic Materials

Tomoki Terasako,† Daisuke Saito, Keisuke Taira, Atsushi Nishinaka, Tomoya Yamaguchi, and Sho Shirakata
Faculty of Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan
(Received 10 October 2008; Accepted 4 January 2009; Published 7 February 2009)

A variety of vertically aligned ZnO nanostructures, such as nanorods, pencil-like nanorods and nanowalls, was successfully grown on sapphire substrates coated with Au nanocolloidal solutions by atmospheric-pressure CVD using Zn powder and H₂O as source materials. Shapes of the nanorods grown on the sapphire substrates coated with the diluted solution of enhanced metalorganic decomposition for NiO film depended strongly on degree of dilution of the solution. Possibility of diameter control using the Ni particles embedding in zeolite supports as catalytic material was also found. [DOI: 10.1380/ejssnt.2009.78]

Keywords: Zinc oxide; Nano-wires; Catalysis; Chemical vapor deposition; Scanning electron microscope; X-ray diffraction; Photo luminescence

I. INTRODUCTION

Zinc oxide (ZnO) is one of the promising materials for ultraviolet-blue light emitting devices because of its bandgap energy of 3.37 eV and exciton binding energy of 60 meV. Recently, nanoscale low dimensional materials have attracted much attention because of their importance in basic scientific research and technological application [1–4]. A variety of ZnO nanostructures, such as nanowires (NWs), nanorods (NRs) and nanobelts (NBs), have been synthesized using various growth techniques. Among these growth techniques, a CVD method utilizing vapor-liquid-solid (VLS) growth mechanism is suitable for positioning and size control of nanostructures. The CVD method using a mixture of ZnO and graphite powders has been widely used for obtaining ZnO NWs with a high crystalline quality [5–7]. It is well known that structural, optical and electrical properties of undoped ZnO are strongly dependent on the intrinsic defects introduced by the deviation from the stoichiometric composition. For the CVD methods using ZnO powder as the source material, the stoichiometry control is considered to be difficult. We believe that the best way to achieve the accurate stoichiometry control in CVD is to separate the Zn and O source materials completely and to control the fed ratio of O to Zn with good precision. Among the several promising O source materials, water (H₂O) is low-cost and convenient. In our previous paper, the successful growth has been reported for ZnO NWs on SiO₂/Si(100) substrate coated with Ni particles by atmospheric-pressure CVD (AP-CVD) using ZnCl₂ and H₂O as source materials has been reported. The source fed ratio of ZnCl₂ to H₂O was found to affect the growth mechanism of ZnO NWs, resulting in difference in NW shape [8].

The achievement of the shape control of ZnO nanostructures has a great importance on their device applications. Therefore, in this paper, the possibility of shape controlled growth of ZnO nanostructures has been studied by means of the AP-CVD method using the Zn powder and H₂O as source materials. Results are discussed in terms of catalyst, substrate, and growth condition involving substrate temperature (Tₛ) and source fed ratio of H₂O to Zn. To avoid the coalescence between adjacent catalyst particles resulting in inhomogeneous size distribution, diameter controlled growths of single- and double-walled carbon nanotubes have been carried out using the catalytic particles embedding in nanoscale porous of zeolite supports [9, 10]. Possibility of diameter control of ZnO nanowires utilizing nanoscale porous in zeolite supports is also discussed.

II. EXPERIMENTAL

Nanostructures of ZnO were grown on a p-type Si(100) wafer with a thermally formed SiO₂ layer (approximately 45 nm in thickness) on c- and a-plane sapphire substrates. The ethanol solution of Au nanocolloids (Nippon Paint, Fine Sphere E-001) (denoted by “Au nanocolloidal solution”) with a concentration of 0.5 wt% and the solution of enhanced metalorganic decomposition (EMOD) for NiO film (NiO-EMOD) (Symmetric, SYM-NI05) diluted with ethanol were used as catalytic materials. These catalytic materials were coated on the substrates by spin coating (1500-3000rpm, 15-30sec).

In addition to these catalytic materials, Ni particles embedding in zeolite supports were also used as a catalyst. The catalytic solution of Ni(NO₃)₆H₂O (Nacalai Tesque, purity of 98%) dissolved in an ethanol (~26.4 μmol/ml) was mixed with the zeolite support (Zeolyst International, Y-type) and stirred to obtain the resultant semisolid form. This semisolid mixture was kept at 140°C for ten hours and then ground into a fine powder. The ethanol solution of the powder was dropped on the SiO₂/Si (100) substrate heated at 80°C in air.

The CVD system was the same as that used in our previous paper [8]. The growth reactor was a quartz tube (1000 mm in length and 35 mm in diameter). The horizontal furnace consisted of two temperature zones; one was for heating the substrate and the other for vaporizing high purity Zn powder (Sigma Aldrich, purity 99.995%). Substrate temperature (Tₛ) was varied in the range from 725 to 950°C. Source temperatures of Zn (TₛZn) and H₂O (TₛH₂O) were kept at 700°C and 54°C, respectively. The H₂O vapor was transported into the reactor by nitrogen carrier gas. To avoid the condensation of H₂O vapor, the stainless tube between the vaporizer and the growth reac-

†This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-5), Waseda University, Japan, 9-13 November, 2008.
†Corresponding author: terasako@eng.ehime-u.ac.jp
TABLE I: Growth conditions for ZnO nanostructures on c-plane sapphire substrates coated with the Au nanocolloidal solution of 0.5wt%.

| Sample Number | $T_S$ (°C) | $T_{Zn}$ (°C) | $F_{Zn}$ (sccm) | $T_{H2O}$ (°C) | $F_{H2O}$ (sccm) |
|---------------|------------|---------------|----------------|----------------|-----------------|
| #1            | 875        | 700           | 20             | 54             | 100             |
| #2            | 900        | 700           | 20             | 54             | 60              |
| #3            | 950        | 700           | 20             | 54             | 100             |
| #4            | 925        | 700           | 20             | 54             | 140             |

The crystallographic structure was characterized by the X-ray diffraction (XRD) method using Cu Kα radiation with a conventional θ-2θ goniometer (Philips, PW1820/00). Surface morphology and film thickness were examined by use of a scanning electron microscope (SEM; Hitachi, S-3100H) under an acceleration voltage of 200kV and selected area electron diffraction (SAED). Photoluminescence (PL) measurements were carried out at room temperature (RT). The excitation light source for PL measurements was the 325 nm line from a He-Cd laser (Kimmion, IK3052R-BR, Output: 5mW). PL from the sample was dispersed and detected by high resolution fiber multichannel spectrometer (Ocean Optics, HR2000, Grating: 600 lines blazed at 400 nm, Detector: 2048 pixel linear CCD array).

### III. RESULTS AND DISCUSSION

#### A. Nanostructures on sapphire substrates coated with Au nanocolloidal solution

Figure 1 shows XRD patterns of four samples grown on the c-plane sapphire substrates coated with Au nanocolloidal solution of 0.5wt% under the conditions shown in Table I. The XRD pattern for the sample #1 exhibits (002), (101), (110) and (004) diffraction lines of ZnO with the hexagonal wurtzite structure. The excitation light source for PL measurements was the 325 nm line from a He-Cd laser (Kimmion, IK3052R-BR, Output: 5mW). PL from the sample was dispersed and detected by high resolution fiber multichannel spectrometer (Ocean Optics, HR2000, Grating: 600 lines blazed at 400 nm, Detector: 2048 pixel linear CCD array).

NRs are in the range from 180 to 500 nm. For the sample #3, NRs are found on the pyramidal structures. The NRs are 120-180 nm in diameter and the pyramidal structures are several microns in base. These pencil-like nanostructures are denoted hereafter by nanopencils (NPs). The (006) diffraction line of sapphire cannot be observed in the XRD pattern for sample #3. This is because the surface of the sapphire substrate was completely covered with the ZnO layer composed of the pyramidal structures. Nanostructures observed on the sample #4 are composed of walls and NRs. The walls are 400-800 nm in thickness and 2 to 8 microns in height. The NRs can be observed on wall nodes. These wall-like nanostructures are similar to those observed and named nanowalls by Ng et al. [11]. In the present study, the nanowalls (denoted hereafter by NWLs) tended to be observed on the samples grown at high $T_S$ and under high source fed ratio of H$_2$O to Zn. Taking into account this tendency, the appearance of the NWLs is attributed to the surface migration of Au nanoparticles followed by the formation of 2D network pattern with increasing $T_S$.

Systematical growth experiments revealed that the substrate temperature higher than 900°C is required for fabrication of vertically aligned NRs. However, it was also clarified that both the tapering of NRs and the formation of NPs are strongly enhanced at high $T_S$. To give a more quantitative description of the tapering of the NRs, Wang et al. defined the tapering parameter $\sigma$ as

$$ \sigma = \frac{d_1 - d_2}{2L}, $$

where $L$ is the length of the NW, and $d_1$ and $d_2$ are the diameters of the NW at its bottom and tip, respectively [12]. We have extended the tapering parameter to the NPs as shown in the inset of Fig. 3. In Fig. 3, the parameter $\sigma$ is plotted on a logarithmic scale as a function of reciprocal substrate temperature, 1000/$T_S$, for the NRs grown...
on the sapphire substrates coated with the Au nanocolloidal solution of 0.5wt%. Regardless of differences in source fed ratio of H$_2$O to Zn and substrate, the parameter $\sigma$ can be expressed approximately by an exponential function of the reciprocal substrate temperature $1/T_S$ as $\sigma \propto \exp(-4.6 \times 10^4/T_S)$. Temperature dependence of $\sigma$ for our ZnO NRs is stronger than that for Al-catalysed Si NWs, $\sigma \propto \exp(-2 \times 10^4/T_S)$, reported by Wang et al.

Simultaneously two types of main growth mechanisms are in progress; one is the axial growth and the other is the radial growth. The axial growth is caused by the VLS mechanism through the catalyst. On the other hand, the radial growth can be regarded as the film growth mechanism on the NR’s side wall. Shapes of the NRs are determined by the competition between the axial and radial growths [13]. The tapering parameter $\sigma$ can be expressed as the ratio of the radial growth rate to the axial growth rate [12]. Therefore, we believe that the strong temperature dependence of $\sigma$ for our ZnO NRs is attributed to the rapid increase in radial growth rate with increasing $T_S$. The influence of the high radial growth rate on the NW growth will be also described in subsection 3.C.

Figure 4 shows PL spectra of the nanostructures with different shapes. All the PL spectra are composed of a near-band-edge (NBE) emission at 3.2-3.3eV and a green band (GB) emission at 2.4eV. PL spectra of the NRs grown at $T_S=875$ and 900$^\circ$C are dominated by the NBE emission, while those of both the NPs and NWLs grown at $T_S=950$C show the strong GB emission. It can be noticed that the nanostructures grown at higher substrate temperature tend to show the strong GB emission. Several researchers suggested that oxygen vacancy (V$_O$) is responsible for the GB emission [14, 15]. Therefore, the increase in $T_S$ contributes not only to the change in shape, but also to the increase in V$_O$ concentration. It can be easily found for samples #3 and #4 that the NBE emission is composed of two peaks. The relative intensity between the two peaks strongly depends on the incidence angle of the excitation light. This fact implies that the luminescence centers related to the two peaks have different polarization dependence. The influence of the difference in polarization dependence between two peaks may
FIG. 4: Photoluminescence spectra of nanostructures with different shapes grown under the conditions shown in Table I ((a) tilted-nanorods (NRs), (b) NRs, (c) nanopencils (NPs) and (d) nanowalls (NWLs)).

data contribute to the difference in peak energy of the NBE emission between samples #1 and #2. The details of the NBE emission observed on the nanostructures will be given elsewhere.

B. Nanostructures on sapphire substrates coated with diluted NiO-EMOD solution

Figures 5(a) and 5(b) show SEM images of samples #5 and #6 grown under the conditions shown in Table II. Differences in growth condition between the samples #5 and #6 are concentration of catalytic solution and types of substrate. In Fig. 5(a), all of the NWs observed on the sample #5 bent and exhibit rounded particles on their tips, indicating that these NWs were grown by the VLS mechanism. On the other hand, NRs observed on the sample #6 shown in Fig. 5(b) have straight and conical shape. When the same mixture of NiO-EMOD solution and ethanol (volume ratio of 1:6) was used as catalyst, NRs grown on the c-plane sapphire substrate resembled to those on the a-plane sapphire substrate (#6) in their shapes and diameters. Therefore, the remarkable difference between the NRs obtained on the sample #5 and those on the sample #6 is attributed to the difference in concentration of the NiO-EMOD solution diluted with ethanol. This result suggests that the concentration of catalytic solution is also one of the important factors for controlling the NR shape.

FIG. 5: Scanning electron microscope images (tilt 30°) of (a) sample #5 and (b) sample #6 grown under the conditions shown in Table II.

FIG. 6: (a) Low-magnification scanning electron microscope (SEM) image of ZnO NWs grown on the SiO$_2$/Si(100) substrate coated with the ethanol solution of Ni(NO$_3$)$_6$H$_2$O. (b) Low- and (c) high-magnification SEM and (d) low- and (e) high-magnification transmission electron microscope images of ZnO NWs grown on the SiO$_2$/Si(100) substrate coated with the zeolites embedding Ni particles. The inset in (e) shows a selective area electron diffraction pattern of the corresponding ZnO NW. The values of $T_S$, $T_{Zn}$, $T_{H_2O}$, $F_{Zn}$, and $F_{H_2O}$ are 700°C, 700°C, 54°C, 120 sccm and 120 sccm, respectively.
TABLE II: Growth conditions for ZnO nanorods on sapphire substrates coated with mixtures of NiO-EMOD solution and ethanol.

| Sample Number | Volume ratio NiO-EMOD : Ethanol | Substrate | $T_s$ (°C) | $T_{Zn}$ (°C) | $F_{Zn}$ (sccm) | $T_{H2O}$ (°C) | $F_{H2O}$ (sccm) |
|---------------|---------------------------------|-----------|-----------|-------------|----------------|--------------|----------------|
| #5           | 1:1                             | c-plane sapphire | 900       | 700         | 15             | 54           | 100           |
| #6           | 1:6                             | a-plane sapphire |           |             |                |              |               |

C. Diameter control utilizing zeolite

Figure 6(a) shows a low-magnification SEM image of NWs grown on the SiO$_2$/Si(100) substrate coated directly with the ethanol solution of Ni(NO$_3$)$_6$H$_2$O (denoted by #7). Figures 6(b) and 6(c) show low- and high-magnification SEM micrographs of ZnO NWs grown on the substrate coated with the zeolite supports embedding Ni particles (denoted by #8). For both the samples, the values of $T_s$, $T_{Zn}$, $T_{H2O}$, $F_{Zn}$, $F_{H2O}$ are 700°C, 700°C, 54°C, 120 sccm and 120 sccm, respectively. Figure 7 shows histograms of diameters for NWs of samples #7 and #8 together with that for the Ni particles on the SiO$_2$/Si(100) substrate. As shown in Figure 7(a), diameter distribution of the Ni particles is very wide and up to 4200 nm because of the coalescence adjacent Ni particles at elevated temperature. Diameters of NWs observed on the sample #7 are in the range from 50 to 600 nm as shown in Fig. 7(b), suggesting that only the Ni particles with smaller diameters were selectively used as catalysts.

As shown in Fig. 6(b), NWs are found only on the substrate surface coated with the zeolite supports embedding Ni particles. Diameters of NWs observed on the sample #8 are in the range from 20 to 70 nm (Figs. 6(c) and 7(c)), which are extremely small in comparison with those on the sample #7 (Figs. 6(a) and 7(b)). The length is up to 10 μm and the obtained highest aspect ratio is 170. The XRD pattern of the sample #8 showed (100), (002) and (101) diffraction lines of hexagonal ZnO, indicating successful growth of ZnO NWs. Figure 6(e) shows lattice fringes and the corresponding SAED pattern of a straight NW indicated by the arrow in Fig. 6(d). The SAED pattern exhibits sharp diffraction spots, indicating that the NW is of single crystalline phase. The spacing of $\sim$0.28nm between the adjacent lattice planes corresponds to the distance between two {100} crystal planes. A PL spectrum of the sample #8 exhibited a dominant NBE emission (the intensity of the NBE emission relative to that of the GB emission is $\sim$14), suggesting the good crystalline quality of NWs.

This result indicates the usefulness of Ni particles embedded in zeolite as catalyst for controlling the NW diameter. Unfortunately we have no available data on distribution of pore diameters in the zeolite. Typical pore diameter in Y-type zeolite is 2.5 nm [9]. Therefore, the diameters of NWs grown by the Ni particles embedded in zeolite are about 8 to 28 times larger than the pore diameter in the zeolite. If the Ni particle was completely embedded in the pores in the zeolite, then the diameter of NWs would become equivalent to that of the pore size. As described above, both the axial and radial growths progress simultaneously during the NW growth process. The appearance of the NWs with diameters larger than...
the pore sizes in the zeollite are probably due to the significant contribution of radial growth mentioned in subsection 3.A.

IV. CONCLUSIONS

Growth experiments of ZnO nanostructures by atmospheric-pressure CVD using Zn and H\textsubscript{2}O as source materials were done by utilizing various catalysts and various substrates. It was clarified that various types of vertically aligned nanostructures, such as nanorods, nanopencils and nanowalls, can be grown on sapphire substrates coated with the Au nanocolloidal solution by adjusting substrate temperature and source fed ratio of H\textsubscript{2}O to Zn. The shapes of the NRs grown on sapphire substrates coated with the diluted solution of enhanced metalorganic decomposition for NiO film depended strongly on degree of dilution of the solution. The use of Ni particles embedding in zeolite support as catalyst was found to be effective for achieving diameter control of nanowires.

Acknowledgments

The authors would like to thank Mr. A. Miyata for his help with the experiments. This study is supported by Grants-in-Aid for Scientific Research C, ‘KAKENHI’ (No. 20510107).

[1] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, and H. Yan, Adv. Mater. 15, 353 (2003).
[2] J. G. Lu, P. Chang, and Z. Fan, Mater. Sci. Engin. R 52, 49 (2006).
[3] H. J. Fan, P. Werner, and M. Zacharias, Small 2, 700 (2006).
[4] C. M. Lieber and Z. L. Wang, MRS Bulletin 32, 99 (2007).
[5] M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, Adv. Mater. 13, 113 (2001).
[6] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, and H.-J. Choi, Adv. Funct. Mater. 12, 323 (2002).
[7] C. Geng, Y. Jiang, Y. Yao, X. Meng, J. A. Zapien, C. S. Lee, Y. Lifshitz, and S. T. Lee, Adv. Funct. Mater. 14, 589 (2004).
[8] T. Terasako and S. Shirakata: Jpn. J. Appl. Phys. 44, L1410 (2005).
[9] K. Mukhopadhyay, A. Koshino, T. Sugai, N. Tanaka, H. Shinohara, Z. Konya, and J. B. Nagy, Chem. Phys. Lett. 303, 117 (1999).
[10] T. Hiraoka, T. Kawakubo, J. Kimura, R. Taniguchi, A. Okamoto, T. Okazaki, T. Sugai, Y. Ozeki, M. Yoshikawa, and H. Shinohara, Chem. Phys. Lett. 382, 679 (2003).
[11] H. T. Ng, J. Li, M. K. Smith, P. Nguyen, A. Cassell, J. Han, and M. Meyyappan, Science 300, 1249 (2003).
[12] Y. Wang, V. Schmidt, A. Senz, and U. Gösele, Nat. Nanotechnol. 1, 186 (2006).
[13] J. Johansson, Nat. Nanotechnol. 2, 534 (2007).
[14] K. Vanheusden, W. L. Warren, C. H. Seager, D. R. Tal- lant, J. A. Voigt, and B. E. Gnade, J. Appl. Phys. 79, 7983 (1996).
[15] F. H. Leiter, H. P. Alves, A. Hofstaetter, D. M. Hofmann, and K. Mayer, Phys. Stat. Sol. B 226, R4 (2001).