Growth Behaviors of ZnO Nanorods Grown with the Sn-Based Bilayer Catalyst-Covered Substrates

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The growth of ZnO nanorods performed at 700°C with the mixture of Zn and ZnO as the Zn source was investigated by having the catalysts in bilayer configurations of Sn (top)/Au (bottom), Sn/Al, Sn/Ni, and Sn/In. These catalyst layers were preannealed at 700°C or 850°C in a gas mixture of argon and hydrogen. The variations in the process parameters are to give the modulations in growing ZnO rods for the purpose of investigating the growth behaviors. The results show that the different compositions and configurations of bilayer catalysts can lead to different reactions and interdiffusions or in different kinetic performance, which will produce different sizes and states of catalyst templates for growing different sizes of the ZnO rods. The small-diameter ZnO nanorods with a hexagonal cross-section at the size of 70–150 nm were obtained from the Sn/Ni catalyst systems preannealed at 850°C.

1. Introduction

Zinc oxide (ZnO) with a wide band gap of 3.37 eV and large exciton-binding energy (60 meV) has been an attractive semiconductor for optoelectronic applications in light emitting diodes and laser diodes at room temperature. Nanometer scale, one-dimensional (1D) materials, such as nanowires (NWs), nanorods, nanobelts, and nanotubes, have become of great interest due to their importance in basic scientific research, and potential technological applications in nanolaser, field emission devices, photovoltaic, piezoelectric transducer, photocatalysts, chemical and biosensors, and so forth [1, 2].

Vapor phase-grown one-dimensional (1D) ZnO nanomaterials were mainly obtained by using the Zn and Zn+ZnO sources with the growth temperatures at 650°C–900°C [3–6], the ZnO+C source at 850°C–1100°C [7, 8], and the diethyl zinc source at 350–500°C [9, 10]. 1D ZnO can grow at the uncoated substrates with the self-catalytic vapor-liquid-solid (VLS) growth mechanism. The major catalysts used on the coated substrates to grow 1D ZnO are gold, nickel, and tin. VLS mechanism has been related to the growth of 1D ZnO with catalysts on its tips, and it is the vapor-solid (VS) growth mechanism for those without catalysts on tips. Although Au catalysts played an important role in forming the 1D ZnO, some grown 1D ZnO had the Au droplets [5, 7], and some had no catalysts on the tips [11, 12]. Ni was also used as a catalyst on the coated substrates. Umar et al. grew hexagonal-shaped ZnO nanorods at 500°C–550°C in an oxygen atmosphere on preannealed Ni-coated substrates with the Zn powder as a source material [3]. The Sn-based catalysts are the focus of this study for growing ZnO rods. 1D ZnO grown above 1000°C on the uncoated substrates with the mixture of ZnO and SnO2 or Sn as source materials has pure Sn droplets observed on tips of nanowires [13–15]. These Sn droplets on the tips of ZnO NWs had the sizes 2-fold larger than those of ZnO rods. If 1D nanomaterials were grown on the Au-coated substrates with the mixture of ZnO and SnO2 powders as a source material at 1000°C, Zn2SnO4 nanowires with an inverse spinel structure were obtained [16, 17].

In the previous report, we had grown 1D ZnO nanorods on the untreated or preannealed bilayer catalyst-covered substrates to explore their growth behaviors and micromechanisms [18]. Three kinds of the bilayer catalysts were Au (the top layer)/Al (the bottom layer), Au/Ni, and Au/In or
Figure 1: Surface morphologies of ZnO grown at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C for 2 h on Au-coated substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1.

Figure 2: Surface morphologies of ZnO grown at 700°C for 2 h on Au-coated substrates by thermal evaporation with a Zn mixture of Zn and ZnO in weight ratios of (a) 2:1, (b) 1:1, and (c) 1:2.
Figure 3: Surface morphologies of ZnO grown at 700°C for 2 h on (a) Al-, (b) Ni-, (c) In-, and (d) Sn-sputtering coated substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1.

Figure 4: Surface morphologies of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/Au substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1.
the Au-based bilayer catalysts. The results indicated that the catalyst-confined nanowire growth via the VS growth mechanism was controlled by the size of catalysts, which was adjusted by alloying or catalyst reactions to change the surface tension and surface energy of the catalysts. There are few studies about the growth of hexagonal 1D ZnO on the bilayer catalyst substrates with Sn as the top layer or on the Sn-based substrates. Sn has a low melting temperature of 232 °C and exists as a liquid at our growth condition of 700 °C. It has very different behaviors to those grown on the bilayer substrates with the Au catalyst on the top layer. After we have some knowledge about the growth on the Au-based systems, the investigations of the growth of hexagonal ZnO rods on the Sn-based substrates become interesting.

The purpose of this study is to study the states of bilayer catalysts on the growth micromechanism of 1D ZnO by deliberately having different bilayer catalyst configurations with an Sn top layer and having different preannealing treatments. By differentiating and understanding the different 1D ZnO growth behaviors, the growth of 1D ZnO is expected to have a better control.

2. Experimental

ZnO nanowires were grown at 600–900 °C for 2 h on the catalyst-coated Si wafer substrates under a mixture flow of 10-sccm (standard cubic centimeter per minute) O2 and 200-sccm argon by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1 : 1. Other Zn sources, for example, Zn, ZnO, ZnCl2, Zn+ZnCl2, ZnO+ZnCl2, and Zn+ZnCl2+ZnO, were also used. The Zinc source was put nearby the substrate. Other Zn sources, for example, Zn, ZnO, ZnCl2, Zn+ZnCl2, ZnO+ZnCl2, and Zn+ZnCl2+ZnO, were also used. Single-layer catalysts of Au, Al, Ni, In, and Sn were deposited on Si wafer substrates by d.c. (direct current) magnetron sputtering. For the bilayer catalysts, there were one top layer A and one bottom layer B, which was symbolized as A/B. In this study, the A layer was fixed with Sn and the four constituted systems were Sn/Au, Su/Al, Sn/Ni, and Sn/In. These metallic catalyst layers had a thickness of 30–60 nm for each. The sputtered bilayer substrates were referred to as the untreated substrates. The effects of preannealing on the bilayer catalyst-covered substrates before the growth of 1D ZnO were studied by executing annealing at 700 °C and 850 °C for 30 min in a tube furnace under the atmosphere of argon and hydrogen, which were referred as 700 °C and 850 °C preannealing, respectively. The phase formation of 1D ZnO was analyzed by X-ray diffraction (XRD, Rigaku D/Max-RC, Japan). Scanning electron microscopes (SEM, JEOL JSM 6500F, Japan; Cambridge S360, UK) were used to observe the growth morphology. Microstructural characterization of nanowires was conducted by a transmission electron microscope (TEM, FEI Tecnai F20G², The Netherlands).
Figure 6: Surface morphologies of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/Ni substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1.

Figure 1 shows surface morphologies of ZnO grown at (a) 600°C, (b) 700°C, (c) 800°C, and (d) 900°C for 2 h on Au-coated substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1. The growth temperature of 700°C was enough to form ZnO nanowires with a diameter of 100–120 nm and the length of hundreds of microns. The mixture of submicron-sized ZnO rods and ZnO nanorods was observed at growth temperature of 600°C. Microsized ZnO polycrystalline layers were obtained at 900°C. The growth temperature of 700°C was chosen for the following experiments.

Figure 2 shows surface morphologies of ZnO grown at 700°C for 2 h on Au-coated substrates by thermal evaporation with a Zn mixture of Zn and ZnO in weight ratios of (a) 2:1, (b) 1:1, and (c) 1:2. Hexagonal-shaped ZnO microrods with a diameter of 1.5–3.5 μm were obtained at the Zn/ZnO ratio of 2:1. Similar ZnO rods with a diameter of 300–600 nm were grown at the Zn/ZnO ratio of 1:2. The best condition was at the Zn/ZnO ratio of 1:1 to obtain ZnO nanowires with a diameter of ~100 nm. Different sizes of 1D ZnO were obtained at the different Zn/ZnO ratios. Because these three experiments were conducted on the same type of Au-covered substrates, the sizes of the Au catalysts were expected to be the same. The obtained 1D ZnO in different sizes indicates the Zn/ZnO vapor pressure is important in determining their morphologies. That is the reason why reports with the Zn metal as a source material had different results in nanowires [5] or in nanorods [3, 4]. The other evidence is that the larger sizes of the 1D ZnO will form the hexagonal shape, which will be explained at the next section about the bilayer catalysts.

Before bilayer catalysts with Sn at the top layer were investigated, the effects of unilayer Al-, Ni-, In-, and Sn-sputtered catalysts on the growth of 1D ZnO were tested. Figure 3 displays surface morphologies of ZnO grown at 700°C for 2 h on (a) Al-, (b) Ni-, (c) In-, and (d) Sn-coated substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1. Large-grained ZnO layers were produced at the Al- and In-covered substrates. Nanopencils were obtained on the Ni-coated substrates. Among catalysts of Au, Al, Ni, In, and Sn, the sputtering coated Au and Sn films were the two available catalysts for our system to generate 1D ZnO. Sn droplets were observed at the tips of the grown 1D ZnO when Sn or SnO2 was used in a mixture with ZnO powders for an evaporation source [13, 15]. In this work, Sn was directly deposited on substrates, and the grown 1D ZnO had no liquid droplets on its tips.

3.2. Growth of ZnO on Bilayer Catalyst-Covered Substrates.

The energy dispersive spectroscopies equipped on SEM and TEM were used to semiquantitatively analyze the phase composition. Room-temperature photoluminescence (PL) measurements were performed using a 325 nm He-Cd laser as the excitation source.

3. Results and Discussion

3.1. Growth of ZnO on Unilayer Catalyst-Covered Substrates.

To choose the Zn source for thermal evaporation, seven sources were tested at 800°C. The pure zinc produced the ZnO polycrystalline films with a large grain size of 3–10 μm. Au nanoparticles instead of 1D ZnO were observed on substrates when ZnO, ZnCl2, and ZnO+ZnCl2 were used. Loose ZnO grains were obtained with the Zn sources of Zn+ZnCl2 and Zn+ZnCl2+ZnO. The only successful source for this study of growing 1D ZnO was Zn+ZnO. The next step is to find the appropriate growth temperature. The energy dispersive spectroscopies equipped on SEM and TEM were used to semiquantitatively analyze the phase composition. Room-temperature photoluminescence (PL) measurements were performed using a 325 nm He-Cd laser as the excitation source.

The energy dispersive spectroscopies equipped on SEM and TEM were used to semiquantitatively analyze the phase composition. Room-temperature photoluminescence (PL) measurements were performed using a 325 nm He-Cd laser as the excitation source.

3.2. Growth of ZnO on Bilayer Catalyst-Covered Substrates.

The bilayer catalysts sputtered on substrates for the growth of 1D ZnO included Sn/Au, Sn/AI, Sn/Ni, and Sn/In. Figure 4 shows surface morphologies of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/Au substrates by thermal evaporation with
Figure 7: Surface morphologies of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/In substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1. (d) EDS spectrum of the SEM image in (c).

Figure 6 shows surface morphologies of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/Ni substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1. 1D ZnO had sizes of 0.8–2.0 μm and 1.0–2.0 μm in diameter after they were grown on the 700°C and 850°C preannealed substrates, respectively. The diameters of 1D ZnO became larger, and the shape changed to microrods after preannealing at higher temperatures. For the Sn/Au system as an example (Figure 4), different preannealing treatments have led to different ZnO sizes. The untreated Sn/Au system can produce the ZnO rods with a uniform diameter, while the system preannealed at 850°C obtained hexagonal rods with different sizes. Different preannealing treatments on the bilayer catalyst-covered substrates are to change the size, shape, or surface energy of catalysts by alloying, interdiffusion, or reactions of the bilayer components.

Figure 5 shows surface morphologies of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/Al substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1. ZnO nanorods with a diameter of 1.0–2.0 μm had a hexagonal shape at its cross-section. The 700°C and 850°C preannealed substrates grew nanorods of 150–500 nm and 150–300 nm in diameter, respectively. Figure 5(d) displays the X-ray diffraction patterns of ZnO nanorods grown on three types of Sn/Al substrates. All the three typed 1D ZnO with a wurtzite structure had the preferred growth direction of [0002].
Figure 8: Photoluminescence spectra of ZnO grown at 700°C for 2 h on (a) untreated, (b) 700°C preannealed, and (c) 850°C preannealed Sn/Al substrates by thermal evaporation with a Zn mixture of Zn and ZnO in a weight ratio of 1:1.

Figure 7(d) shows the EDS spectrum of the 1D ZnO in Figure 7(c). Only Zn and O were detected without other impurities.

Preannealing on the Sn/Au-covered substrates led to the micrometer-sized ZnO rods with a hexagonal shape, while the rods obtained from the Sn/Al-, Sn/Ni-, and Sn/In-coated ones had smaller diameters. Furthermore, most of the ZnO rods grown on the bilayer catalyst-covered substrates...
displayed a hexagonal cross-section without the evidence of catalyst droplets at their ends, which indicates that a vapor-solid growth mechanism is preferred. The changes in the sizes of ZnO rods with the different preannealing treatments on different catalyst systems indicate the formation of different sizes of catalyst templates due to the considerations of the surface/interfacial energy. These different-sized templates provide the sites for the catalyst-confined growth via the VS growth mechanism. A similar approach to control diameter has been observed in the unilayer Au catalyst-coated system by varying the Au layer thickness [19]. About 700–1500 nm diameter has been observed in the unilayer Au catalyst-

plates provide the sites for the catalyst-confined growth via Sn/Ni, and Sn/In systems. The preannealing treatment refers d.c. sputtering includes the Sn (top)/Au(bottom), Sn/Al, Sn/Ni, and Sn/In systems. The preannealing treatment refers to the annealing of catalysts at 700°C or 800°C in the gas mixture of hydrogen and nitrogen before the substrates are put into the other furnace to grow 1D ZnO. The bilayer catalyst method has helped us to face growth micromechanism in order to distinguish the different sizes of rods at different catalyst systems and different process conditions. The growth behaviors of Sn-based catalyst systems are strongly affected by the second component located as the bottom layer. The size of the 1D ZnO from the Sn/Au system becomes larger after preannealing, but it becomes smaller for other catalyst systems. The different behaviors are caused by interdiffusion, reactions, surface tension, and the ability of making catalyst spheroids. The smaller-diameter ZnO nanorods with a hexagonal cross-section at the size of 70–150 nm were obtained from the Sn/Ni catalyst systems preannealed at 850°C.

Our ZnO rods have a vapor-solid growth mechanism, different from those with the Sn droplets on the tips [13, 15]. In our experiments, the supplied oxygen and the vaporizing zinc vapor are participating in the growth of 1D ZnO at the growth temperature of 700°C. Because there is no solubility between Zn and Sn from the binary Zn-Sn phase diagram, the Zn vapor after adsorbed on the bilayer Sn/Au catalysts does not dissolve into Sn-Au melt. The adsorbed Zn adatoms will combine with oxygen to form the Zn-O molecules on catalysts. For the reason of considering surface/interfacial energy, the accumulation and stacking of Zn-O molecules on the liquid templates will form the hexagonal plates to obtain the 1D ZnO with a [0001] growth orientation. This orientation is favored when the liquid templates have larger sizes [20]. To support in lowering the surface/interfacial energies, the liquid Sn-Au templates should adjust to provide a surface for the hexagonal nuclei by forming a ZnO/Sn-Au interface to lower the total free energy. The growth of [0001]-oriented ZnO rods on the Sn droplets has shown the interfacial orientation relationship of (020)Sn∥(0001)ZnO and [T01]Sn∥[2T0]ZnO between ZnO rod and Sn particle [14]. The hexagon in cross-section is preferred due to the lattice match between (020)Sn and (0001)ZnO. Our liquid Sn-Au catalyst templates might provide a similar role to obtain hexagonal ZnO rods.

The approach of using the bilayer catalysts to obtain one-dimensional ZnO with the method of thermal evaporation and oxidation has demonstrated the advantages of adjusting the dimension and growth micromechanism of ZnO rods. Further investigations and understanding for catalysts in the alloy state are needed in order to have a better control in growing the ZnO nanorods.

4. Conclusions

Hexagonal ZnO rods have been successfully grown at 700°C on the untreated or the preannealed bilayer catalyst-covered substrates. The bilayer catalysts fabricated by the d.c. sputtering includes the Sn (top)/Au(bottom), Sn/Al, Sn/Ni, and Sn/In systems. The preannealing treatment refers to the annealing of catalysts at 700°C or 800°C in the gas mixture of hydrogen and nitrogen before the substrates are put into the other furnace to grow 1D ZnO. The bilayer catalyst method has helped us to face growth micromechanism in order to distinguish the different sizes of rods at different catalyst systems and different process conditions. The growth behaviors of Sn-based catalyst systems are strongly affected by the second component located as the bottom layer. The size of the 1D ZnO from the Sn/Au system becomes larger after preannealing, but it becomes smaller for other catalyst systems. The different behaviors are caused by interdiffusion, reactions, surface tension, and the ability of making catalyst spheroids. The smaller-diameter ZnO nanorods with a hexagonal cross-section at the size of 70–150 nm were obtained from the Sn/Ni catalyst systems preannealed at 850°C.

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