

Article

Effects of Experimental Configuration on the Morphology of Two-Dimensional ZnO Nanostructures Synthesized by Thermal Chemical-Vapor Deposition

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Abstract: Using two experimental configurations, self-assembled zinc oxide (ZnO) nanostructures including nanoplates, nanosaws, and nanobelts were synthesized by thermal chemical-vapor deposition (CVD), and their morphological properties were investigated. ZnO nanostructures grown on Au-coated Si substrates in a parallel setup revealed highly defined ZnO nanoplates and branched nanowires. ZnO nanostructures grown in a perpendicular setup using Si substrates with and without the Au catalyst exhibited vertically oriented ZnO nanosaws and randomly aligned nanobelts, respectively. In the thermal CVD method, experiment conditions such as oxygen-flow rate, growth temperature, and catalyst, and experimental configurations (i.e., parallel and perpendicular setups) were important parameters to control the morphologies of two-dimensional ZnO nanostructures showing platelike, sawlike, and beltlike shapes.

Keywords: experimental configuration; ZnO nanoplates; ZnO nanosaws; ZnO nanobelts; thermal chemical-vapor deposition; two-dimensional nanostructures

1. Introduction

Zinc oxide (ZnO) has attracted much attention because of its interesting characteristics such as its near-ultraviolet (UV) emission, transparent conductivity, semiconducting property, and piezoelectricity [1–3]. Self-assembled ZnO nanostructures with different morphologies have promising applications in many fields such as nanolasers [4], piezoelectric-power generation [5], gas sensing [6], and solar cells [7] owing to their high photoelectric reaction, large surface area, cost-effective fabrication, and ecofriendly nature. Unusual material properties of ZnO nanostructures with unique morphologies were reported, including the presence of nanobelts [8], nanocages [9], nanocombs [10], and nanoforests [11]. In particular, two-dimensional ZnO nanostructures, such as nanosheets and nanoplates, are advantageous for catalysis and photocatalysis applications due to their high surface-to-volume ratio [12]. The specific surface areas of ZnO nanostructures can be enhanced by controlling their shapes and morphologies.

Various methods were developed to synthesize ZnO nanostructures, including thermal chemical-vapor deposition (CVD) [13], metal-organic CVD [14], the solution process [15], molecular beam epitaxy [16], and laser ablation [17]. Among these methods of growing ZnO nanostructures, the thermal CVD method has received great interest because the growth process is relatively simple,

and the morphology of the nanostructures can easily be tuned by varying experiment parameters such as temperature and oxygen partial pressure.

In most cases of thermal CVD, substrates are placed in a position parallel to the boat with the source powders in a quartz reactor tube. When the temperature of the boat increases, the mixture of ZnO and carbon powders is vaporized, and Zn is formed by a carbothermal reduction process. Zn reacts with oxygen under ambient conditions on the Si substrates, leading to the growth of ZnO nanostructures. Because vapor transport and reactions depend on the position in the reactor tube [18], the location of the substrates has a significant effect on the morphologies of the synthesized nanostructures. In addition, depending on the geometry of the reactor tube, two-dimensional ZnO nanostructures can be observed during thermal CVD growth on Si substrates under specific growth conditions [19,20]. Hence, we examined the influence of experiment setups and selective conditions in thermal CVD on the growth of self-assembled ZnO nanostructures.

A metal catalyst on the substrate surface is typically required for the initiation and guidance of ZnO nanostructure growth in thermal CVD, resulting in vapor-liquid-solid (VLS) [21,22] and vapor-solid (VS) [20,23] mechanisms. On the other hand, catalyst-free growth of two-dimensional ZnO nanostructures by thermal CVD is interesting with respect to cost-effectiveness. VS growth or self-catalyzed growth mechanisms [24,25] are most often used to describe the catalyst-free growth of ZnO nanostructures.

In this study, we investigated the effects of growth conditions on the morphology of catalyst-mediated ZnO nanostructures synthesized by thermal CVD under different experimental configurations, specifically parallel and perpendicular setups. Two-dimensional ZnO nanostructures were prepared by changing oxygen-flow rate from 0.1 to 2.5 sccm, and growth temperature from 700 to 900 °C. Furthermore, the catalyst-free growth of ZnO nanostructures in thermal CVD with a perpendicular setup was investigated in relation to growth temperatures.

2. Experiments

Two-dimensional ZnO nanostructures with different morphologies were grown in a horizontal quartz reactor tube by thermal CVD using two types of experimental configurations, as shown in Figure 1. Parallel and perpendicular setups were classified by the position of substrate to the gas flow. In the parallel setup, the Zn precursor was placed on the upstream side. Distance between substrate and precursor in the parallel setup was fixed at about 7 cm. The substrate in the perpendicular setup vertically faced the precursor at a distance of 4 mm.

Before growing the ZnO nanostructures, for the catalyst-assisted growth of ZnO nanostructures, a gold layer was coated onto the Si substrates by direct-current sputtering. To prepare a Zn precursor, ZnO powder (99.9%, Sigma-Aldrich, Saint Louis, MO, USA) was mixed with graphite powder (99.9%, Sigma-Aldrich, Saint Louis, MO, USA) at a 1:1 weight ratio. The mixed powders were placed in an alumina boat inserted into a quartz tube and placed close to the middle of the furnace. Prior to heating, a furnace system was flushed with inert Ar gas for 1 h to remove contamination and residual gases in the reactor. A heating system was used to increase the temperature inside the furnace. After initially maintaining at room temperature for 1 h, the temperature was raised to the desired growth temperature at a rate of 5 °C/min. After the desired temperature was attained, the growth time of ZnO nanostructures was 1 h. Growth temperature was changed from 700 to 900 °C. During the growth of the ZnO nanostructures, a mixture of Ar and O₂ was introduced toward the right side from the left side in the reactor. The flow rates of Ar and O₂ were measured by flowmeter. O₂ flow rate was varied from 0.1 to 2.5 sccm, while Ar flow rate was maintained at 100 sccm. Finally, after ZnO nanostructure growth, the furnace was turned off and allowed to cool to room temperature.

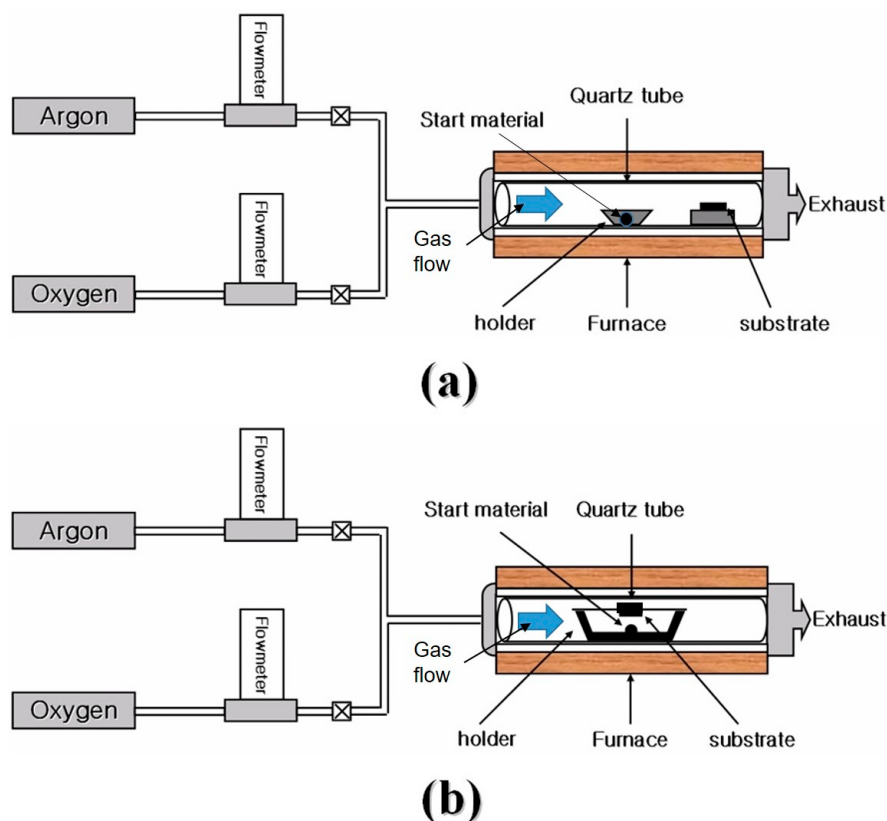


Figure 1. Schematics of thermal chemical-vapor deposition (CVD) setups in this study: (a) parallel and (b) perpendicular setups.

The morphologies of the ZnO nanostructures were observed using a field-emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Tokyo, Japan). To clearly observe the shapes and morphologies of the ZnO nanostructures, acceleration voltage was measured by changing from 10 to 20 kV. Room-temperature photoluminescence (PL, LabRam HR, Horiba, Kyoto, Japan) characteristics of the ZnO nanostructures grown on the Si wafer were measured. In the PL measurement, a 325 nm wavelength He-Cd Laser (30 mW) and a GaAs photomultiplier tube were used for excitation and detection, respectively. X-ray diffraction (XRD, X'Pert MPD, PANalytical, Almelo, Netherlands) using Cu-K α radiation at room temperature was performed in order to investigate the crystal structures of ZnO nanostructures. The 2 θ -2 θ measurement method was used for crystallinity analysis.

3. Results and Discussion

Figure 2 shows FE-SEM images of ZnO nanostructures grown on Au-coated Si substrates at a constant growth temperature of 800 °C in the parallel setup while varying the oxygen-flow rate of the mixed gas with argon and oxygen. As shown in Figure 2a, the ZnO nanostructures grown at an Ar/O₂ flow rate of 120/0.1 sccm had many interconnected or branched nanowires and a few nanoplates. Au nanoparticles were observed at the top of the nanowires, indicating that the growth process of the ZnO nanowires grown at an Ar/O₂ flow rate of 120/0.1 sccm could be explained by the VLS mechanism. However, because no Au particles were observed in the FE-SEM images of the ZnO nanoplates grown at an Ar/O₂ flow rate of 120/0.1 sccm, ZnO nanoplates could have been synthesized by the VS mechanism. Accordingly, from the viewpoint of the VS growth process, ZnO nanoplates were grown by thermally evaporating a precursor, and condensation on the Au catalyst. In Figure 2b, the ZnO nanostructure grown at an Ar/O₂ flow rate of 120/1.0 sccm exhibited highly defined ZnO nanoplates and branched nanowires. As seen in Figure 2c, the ZnO nanostructures grown at an Ar/O₂ flow rate of 120/2.5 sccm showed almost the same number of ZnO nanoplates and

nanowires, displaying irregularly shaped nanostructures. From this result, it can be proposed that excess oxygen gas prohibited nanoplate synthesis during the VS growth process. Due to different oxygen contents in the gas mixtures, different morphological features of the ZnO nanoplates were created. Therefore, we suggest that oxygen concentration in the gas mixture was a crucial parameter to control the morphologies of ZnO nanoplates in the parallel setup.

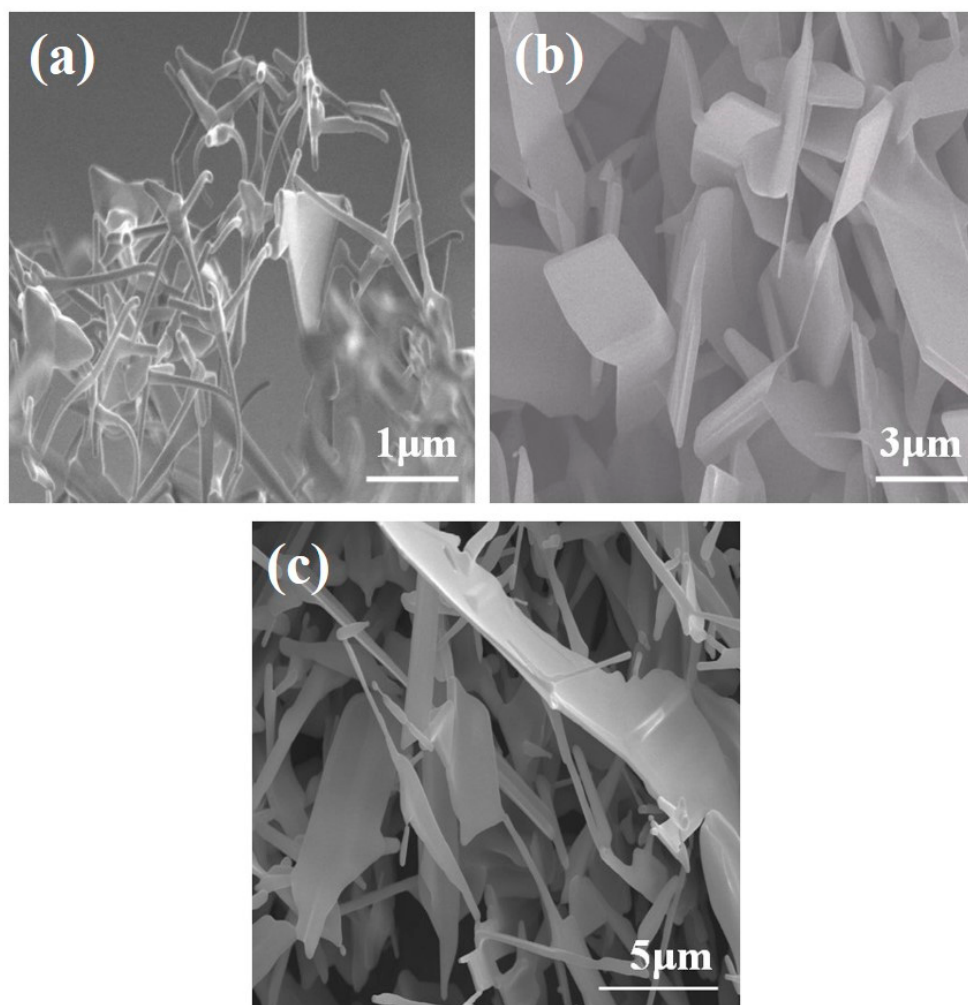


Figure 2. Field-emission scanning-electron-microscope (FE-SEM) images of ZnO nanostructures grown on Au-coated Si substrates at a constant growth temperature of 800 °C in parallel setup with varying Ar/O₂ flow rates in the gas mixture; (a) 120/0.1 sccm, (b) 120/1.0 sccm, and (c) 120/2.5 sccm.

Figure 3 shows the PL spectrum of ZnO nanostructures with nanoplates and branched nanowires grown on Au-coated Si substrates in the parallel setup at an Ar/O₂ flow rate of 120/1.0 sccm. We noted a narrow UV band at 380 nm (3.26 eV) and a broad green band at 570 nm (2.17 eV). UV band emission was due to a near band-edge transition of ZnO nanorods [26]. Green-band emission is caused by the radial recombination of a photogenerated hole with an electron that belongs to singly ionized oxygen vacancy, which was also observed in the bulk ZnO [27]. It was obvious that the green-band emission of the ZnO nanostructures grown at an Ar/O₂ flow rate ratio of 120/2.5 was weaker than that of the ZnO nanostructures grown at an Ar/O₂ flow rate ratio of 120/1.0, resulting from the reduction of oxygen vacancies in the ZnO nanostructures due to the increase of O₂ content in the gas mixture. Thus, the ZnO nanostructure grown on Au-coated Si substrates in the parallel setup was oxygen-deficient nanoplates, exhibiting similar PL properties to the bulk ZnO.

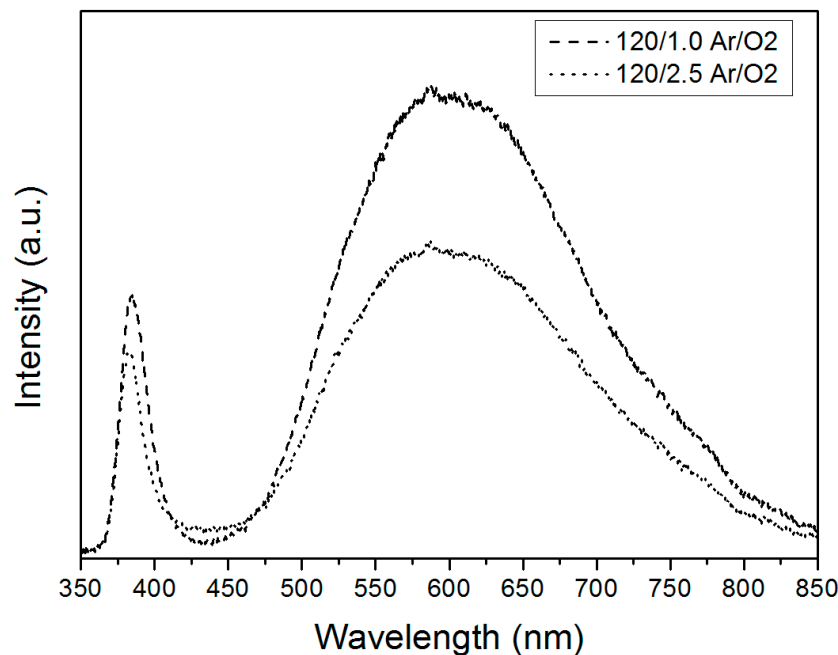


Figure 3. Photoluminescence (PL) spectrum of ZnO nanoplates and branched nanowires grown on Au-coated Si substrates in parallel setup with varying Ar/O₂ flow rates of 120/1.0 sccm (dotted line) and 120/2.5 sccm (dashed line).

Figure 4 shows FE-SEM images of ZnO nanostructures grown in the perpendicular setup on Au-coated Si substrates as a function of growth temperature. According to Figure 4a, the ZnO nanostructures grown at 700 °C had many nanosaws and some nanorods that were randomly oriented. As shown in Figure 4c, ZnO nanostructures grown at 900 °C had many nanowires and a few nanosaws. Contrary to these results, as illustrated in Figure 4b, ZnO nanostructures grown at 800 °C had vertically oriented ZnO nanosaws with a tapered shape. Therefore, growth temperature was a key parameter that could be used to control the morphologies of ZnO nanosaws. It is well known that ZnO nanosaws are synthesized by the catalyzed growth of the Zn-terminated (001) surface, while the O-terminated (001) surface is relatively chemically inactive [28]. Moreover, the morphology of ZnO nanostructures is determined by growth temperature, which is related to surface energy including polarization and termination [29]. As such, it is suggested that a growth temperature of 800 °C resulted in self-catalyzed growth, yielding tapered and vertically aligned nanostructures, as shown in Figure 4b.

Figure 5 shows FE-SEM images of ZnO nanostructures grown in a perpendicular setup on Si substrates without the Au catalyst as a function of growth temperature. As shown in Figure 5a, ZnO nanostructures grown at 700 °C had many nanowires and some nanosheets that were randomly oriented. The ZnO nanostructures grown at 800 °C, as illustrated in Figure 5b, had many nanowires and some ZnO nanobelts that had widths ranging from 1 to 2 µm. As seen in Figure 5c, ZnO nanostructures grown at 900 °C had many nanoplates and a few nanowires. Thus, we can confirm that ZnO nanobelts with wide widths can be synthesized in growth process without introducing a catalyst [30]. In all samples, ZnO nanostructures were randomly oriented because the Au catalyst was not used in the growth process. This is related to the formation of a polycrystal ZnO film without the preferred orientation at an initial growth stage [31]. Therefore, growth temperature in the perpendicular setup without the Au catalyst was an important parameter that could be used to control the morphologies of ZnO nanobelts under suitable growth conditions, such as under specific partial oxygen pressure or with the use of specific substrate-setup positions.

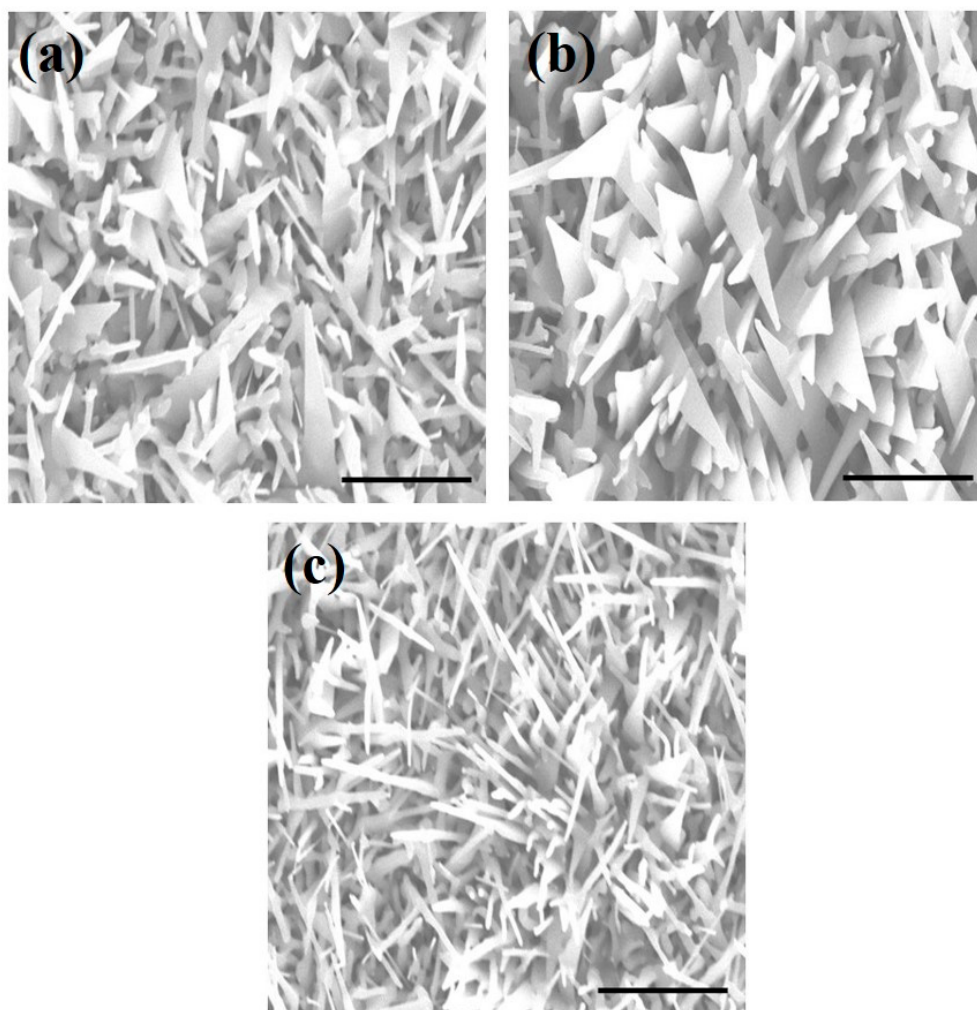


Figure 4. FE-SEM images of ZnO nanostructures grown in perpendicular setup on Au-coated Si substrates as function of growth temperature at Ar/O₂ flow rate of 120/1.0 sccm in gas mixture: (a) 700 °C, (b) 800 °C, and (c) 900 °C. Scale bar is 3 μ m.

It is well known that ZnO nanobelts that show flat top and bottom surfaces $\pm$ (2–10), and side surfaces $\pm$ (001) grow along [010] and occur bending due to strain [30]. Moreover, the morphology of ZnO nanostructures grown without a catalyst can be determined by growth temperature, which is related to the chemical inactivity of the surface and the activation energy of normal VS growth [26]. From these facts, it is suggested that a growth temperature of 800 °C in a perpendicular setup without a catalyst led to normal VS growth, yielding bent and randomly aligned nanostructures.

Hereafter, we consider catalyst-mediated ZnO nanostructures grown under different experiment setups at a growth temperature of 800 °C and an Ar/O₂ flow rate of 120/1.0 sccm. The effect of the Au catalyst on ZnO nanostructure growth during thermal CVD with a perpendicular setup under the same growth conditions is reviewed.

As seen in Figure 2b, in the parallel setup, ZnO nanoplates showing rectangular shapes were grown using two growth processes consisting of two-dimensional filling and one-dimensional branching yielding ZnO nanoplates and branched nanowires. The ZnO nanoplates had widths ranging from 3 to 4 μ m and lengths ranging from 4 to 6 μ m. The thicknesses of the nanoplates and the lengths of the branched nanowires ranged from 300 to 600 nm and 2 to 4 μ m, respectively. However, as shown in Figure 4b, ZnO nanosaws showing triangular shapes were tapered from the bottom on the substrate in the CVD process, and had widths ranging from 200 to 400 nm at their base and about 20 nm at the tip. In contrast, as illustrated in Figure 5b, ZnO nanobelts grown in the perpendicular setup

without the Au catalyst were bent during the CVD growth process and had widths ranging from 1 to 2 μm . The tapered nanosaws exhibited a strongly preferred orientation with respect to the *c* plane, as shown in Figure 4b. Here, we can tell that the parallel setup led to the growth of randomly oriented plate-shaped ZnO nanostructures due to the temperature gradient between source materials and substrates in the quartz tube. However, the perpendicular setup led to the growth of well-defined saw- and belt-shaped nanostructures due to stable temperature distribution between source materials and substrates in the quartz tube. The perpendicular setup, with and without the Au catalyst, caused the growth of vertically aligned ZnO nanosaws and randomly aligned ZnO nanobelts, respectively, on Si substrates.

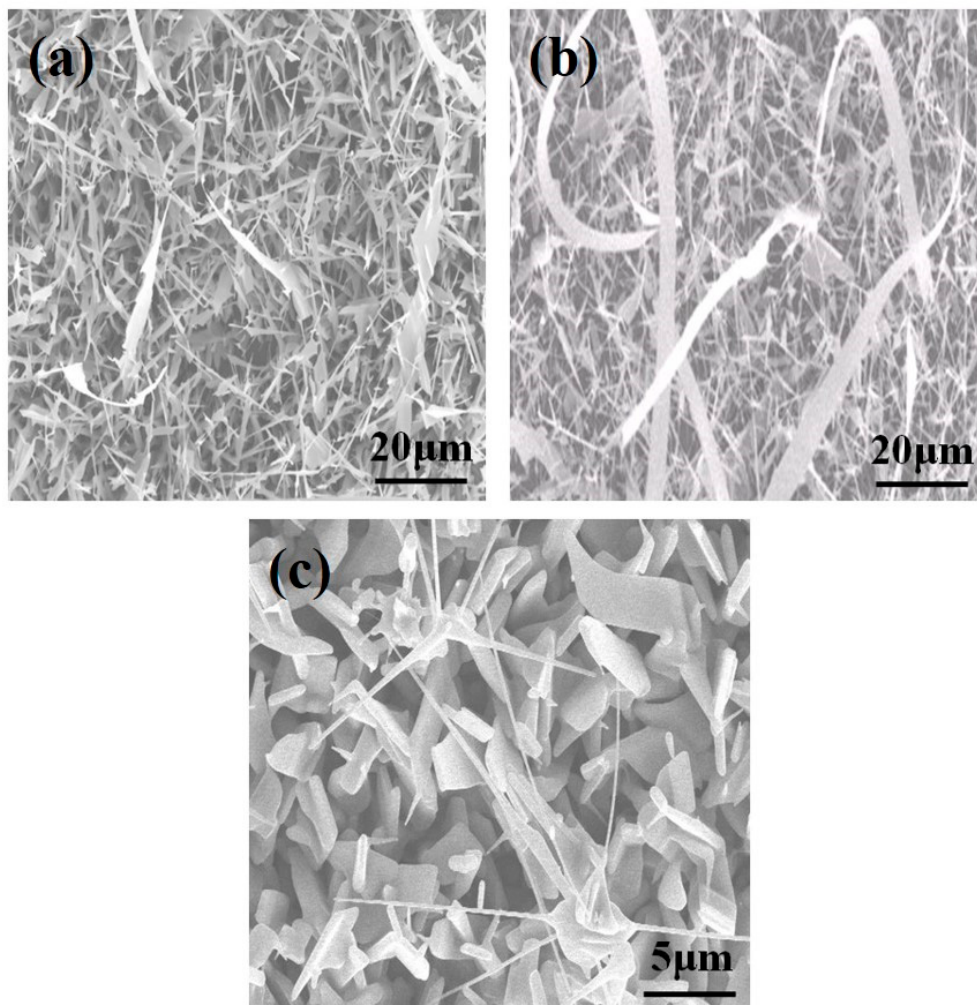


Figure 5. FE-SEM images of ZnO nanostructures grown in perpendicular setup on Si substrates without Au catalyst as function of growth temperature at a Ar/O₂ flow rate of 120/1.0 sccm in gas mixture: (a) 700 °C, (b) 800 °C, and (c) 900 °C.

Figure 6 shows the XRD patterns of the ZnO nanoplates (Figure 2b), nanosaws (Figure 4b), and nanobelts (Figure 5b) grown via the thermal CVD method. The XRD patterns exhibited a large peak at about 69.16° corresponding to the Si substrate. All samples exhibited diffraction peaks of (100), (002), (101), (102), (110), (103), (200), and (112) planes, consistent with the hexagonal wurtzite structure (Joint committee on powder diffraction standards (JCPDS) no. 89-1397). This indicated that morphological changes in the ZnO nanostructures seldom affected the crystal structure. The diffraction peak of the (002) plane for the ZnO nanoplates and nanobelts was weakly observed compared to that of the (101) plane, implying a weakly preferred orientation in the *c*-axis direction. However, a strong

diffraction peak of the (002) plane and a very weak peak of the (101) plane for the ZnO nanosaws were observed, implying highly (002) plane-oriented growth. It is known that, in ZnO, a faster (001) growth direction is due to the higher surface energy of the polar plane. Therefore, a high (002) plane orientation indicated that most of the ZnO nanosaws grew along the (001) direction. In addition, compared to the catalyst-free growth of ZnO nanostructures, the Au catalyst gave rise to the enhancement of a crystalline orientation, as shown in Figures 4–6. This is based on the observation that catalyst-mediated growth led to crystalline nanostructures growing in specific crystallographic directions [32].

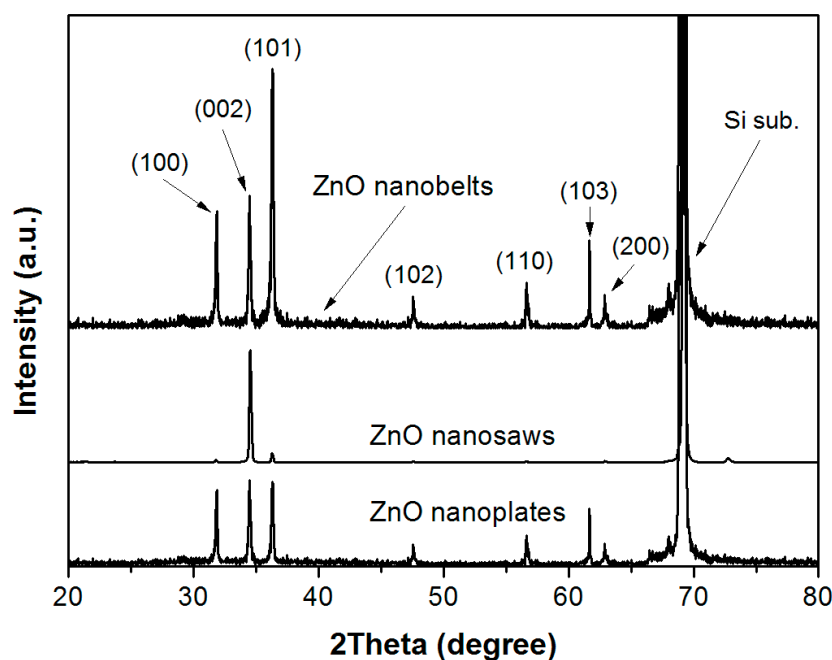


Figure 6. X-ray diffraction (XRD) patterns of ZnO nanoplates, nanosaws, and nanobelts grown under different experiment setups at growth temperature of 800 °C and Ar/O₂ flow rate of 120/1.0 sccm.

4. Conclusions

Two-dimensional ZnO nanostructures showing various shapes were grown under different experiment setups and selective conditions using a thermal CVD method. By varying O₂ flow rate, ZnO nanostructures grown on Au-coated Si substrates in the parallel setup revealed highly defined ZnO nanoplates and branched nanowires, likely as a result of two growth processes: two-dimensional filling and one-dimensional branching. With a growth temperature of 800 °C and an Ar/O₂ flow rate of 120/1.0 sccm, Au-catalyst-mediated ZnO nanostructures grown in the perpendicular setup exhibited vertically oriented ZnO nanosaws that grew from the bottom of the substrate in a tapered shape. ZnO nanostructures grown in the perpendicular setup without the Au catalyst showed bent randomly aligned ZnO nanobelts. The ZnO nanoplates, nanosaws, and nanobelts had hexagonal wurtzite structures, indicating that the morphological changes of ZnO nanostructures seldom affected their crystal structures. It can be concluded that experimental configuration (i.e., a parallel or perpendicular setup) and experiment conditions (e.g., oxygen-flow rate, growth temperature, and catalyst) are key parameters that can be used to control the morphologies of two-dimensional ZnO nanostructures that grow in the thermal CVD method.

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Conflicts of Interest: The authors declare no conflict of interest.

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