# Controlled Growth of ZnO Nanopagoda Arrays with Varied Lamination and Apex Angles

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**ABSTRACT:** Aligned ZnO nanopagoda arrays have been grown on the silicon substrate with ZnO nanorod arrays by a hydrothermal and downward growth process. The concentration of ascorbic acid was used to control the growth direction and the degree of lamination of the ZnO nanostructure with a vastly reduced reaction time (from 24 to 2 h). Low turn-on and threshold fields indicate that ZnO nanopagodas are promising for applications in field emission devices. The ZnO nanopagodas exhibit a very prominent blue shift (10 nm) of UV emission and almost no green emission attributed to singly ionized oxygen vacancies at room temperature. The enhancement in deep-UV optical properties shall be advantageous in applications for nanoscale light-emitting devices. The polar surface concept can be used to understand the ZnO growth mechanism of nanopagodas. The appropriate substrates and reaction conditions lead to the growth of ZnO nanopagoda arrays with wafer-scale production. The large-scale ZnO nanopagoda arrays shall be beneficial in fabricating the novel devices, such as field emitters, ultraviolet lasers, and dye-sensitized solar cells.

## Introduction

Zinc oxide is a versatile material that has demonstrated promising applications in nanodevices such as piezoelectric gated diodes,<sup>1</sup> piezoelectric nanogeneators,<sup>2</sup> photodiodes,<sup>3</sup> photonic crystals,<sup>4</sup> chemical sensors,<sup>5</sup> and solar cells.<sup>6</sup> Wurtzite structure ZnO can be described schematically as a number of alternating planes composed of 4-fold coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions and stacked alternatively along the *c*-axis.<sup>7</sup> The structure produces positively charged [0001]-Zn and negatively charged [0001]-O polar surface, inducing a normal dipole moment and spontaneous polarization as well as a divergence in surface energy. An additional polar surface is  $\{01\overline{1}1\}$ <sup>8</sup> The electrostatic interaction energy and distinct chemical activities of the polar surfaces are conductive to the formation of particular structures, such as nanosprings,<sup>7</sup> nanorings,<sup>9</sup> nanobows,<sup>10</sup> and nanohelices.<sup>11</sup> The polar surface properties had been widely explored for structures produced by thermal evaporation method, but less in structures synthesized with the aqueous chemical growth (ACG) method.<sup>8</sup>

In aqueous chemical growth, oriented nanocrystalline films are deposited on various substrates in aqueous media by heterogeneous nucleation and subsequent growth.<sup>12</sup> The growth method has been demonstrated to synthesize successfully twodimensional arrays of ZnO nanorods,<sup>13</sup> ZnO nanotubes,<sup>14</sup> ZnO nanowires,<sup>15</sup> ferric oxide nanorods,<sup>16</sup> and tin dioxide nanorods.<sup>17</sup> Previous works on hydrothermal processes were focused on the control of patterned growth<sup>12</sup> on various substrates,<sup>15,18</sup> using different reaction reagents<sup>19</sup> and capping reagents<sup>20</sup> to produce ZnO nanostructures with desired morphology. The capping reagents are remarkably effective in controlling the shapes of ZnO nanostructures. For aqueous chemical growth, low temperature and solution-phase synthesis has the potential for low cost and industrial-scale fabrication. The method has proved to be particularly attractive for minimal equipment requirement, low thermal budget, large scale growth, and low selectivity of substrate.

### **Experimental Section**

Si (001) wafer was cleaned ultrasonically for 10 min in ethanol. A thin film of zinc acetate was then coated on the substrate by spinning a layer of solution of 5 mM zinc acetate dihydrate (98%, Aldrich) in ethanol and repeating 10 times. 5-10-nm-thick ZnO seed film was produced after annealing at 300 °C in air for 20 min.<sup>21</sup> The ZnO nanorod layers were grown by an aqueous chemical method in 100 mL aqueous solution containing either 10 mM zinc acetate dihydrate and hexamethylenetetramine (99%, Aldrich) (HMTA) each or 50 mM zinc nitrate hexahydrate (98%, Aldrich) and HMTA each. The substrate with nanorods was placed downward near the surface of reaction solution and heated to about T = 90 °C for 3 h.<sup>21</sup> ZnO nanopagodas were grown by an aqueous chemical and downward growth method in a 100 mL aqueous solution. For the downward growth, the substrate was pasted on the bottom side of a glass plate bridged between two standing glass slides so that it was immersed in but nearly flush with the surface of reactive solution. In the downward growth, the depletion of the precursor is accelerated at the growth surface owing to the gravitational pull of the precursor toward the bottom of the beaker. The solutions contain various equimolar zinc nitrate hexahydrate and HMTA, with the addition of different concentrations of ascorbic acid (99%, Aldrich). The reactions proceeded at T = 90 °C for 2 h. The substrate film was either ZnO seed layer film or ZnO nanorod film.

The ZnO morphology was examined with a field emission scanning electron microscope using a JEOL JSM-6500F SEM operating at 15 kV accelerating voltage. The thickness of ZnO nanostructures was measured by cross section SEM. A JEOL-2010 transmission electron microscope operating at 200 kV was used to examine the microstructures. A Keithley 237 source-measurement unit was used to obtain the current–voltage (I-V) and field emission characteristics. The field emission measurements were carried out in a vacuum chamber with a pressure of  $1 \times 10^{-6}$  torr at room temperature. A copper electrode probe used as an anode with an area of  $3.3 \times 10^{-3}$  cm<sup>2</sup> placed at a distance of 480  $\mu$ m from the tips of the nanopagodas, and it was adjusted by a precision screwmeter with an accuracy of  $\pm 0.1 \ \mu$ m.

#### **Results and Discussion**

Figure 1a shows a SEM image depicting the vertical ZnO nanoneedle arrays grown from equimolar (5 mM) zinc nitrate and HMTA reaction solution by the downward growth method.

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Concentration of ascorbic acid

Figure 1. SEM images of ZnO nanostructures grown on Si wafer precoated with ZnO seed film with (a) 0 mM ( $20^{\circ}$  tilt image), (b) 0.125 mM, (c) 0.1875 mM, and (d) 0.25 mM ascorbic acid in the reaction solution. (e) The schematic illustrating the variation in ZnO nanostructures with the concentration of ascorbic acid in the reaction solution.

The substrates were covered with ZnO seed layer film prepared with a total growth time of 2 h. The diameters and lengths of the nanoneedles are about 20-80 nm and 650-800 nm, respectively. The downward growth method was previously demonstrated to produce the ZnO nanoneedle arrays.<sup>21</sup> With the addition of a small amount of ascorbic acid (0.125 mM), the tapered and laminated ZnO nanostructures, herein called nanopagodas, were formed as shown in Figure 1b. The base diameters and tip widths of laminated nanopagodas are about 70-200 nm and 8-50 nm, respectively. The base diameters and tip widths of ZnO nanopagodas were appreciably changed by the slight variation in the concentration of ascorbic acid. As the concentration of ascorbic acid was increased to 0.1875 mM, the stepwise structure became very pronounced throughout and the nanopagodas have decreased base diameters and very sharp tips, as seen in Figure 1c. The diameters and lengths of the nanopagoda tips are 3-30 nm and 50-300 nm, respectively. Figure 1d shows a SEM image of a sample prepared with the addition of 0.25 mM ascorbic acid. The ZnO nanopagodas were constituted of many thinner ZnO nanoplates with the wider dimension than those seen in Figure 1c. The surface of ZnO nanopagodas became relatively rough, and the stacking of ZnO nanoplates appeared to be less distinct. In cases with ascorbic acid concentrations lower than 0.125 mM, nanoneedles with obtuse tips were formed. Figure 1e shows schematic diagrams illustrating the variation in morphology with the ascorbic acid concentration. The three kinds of laminated nanopagodas with less than 10 layers, between 10 to 30 layers and more than 30 layers are herein designated as thick-layer nanopagodas (0.125 mM), nanopagodas (0.1875 mM), and thin-layer nanopagodas (0.25 mM), respectively.

In previous works, ascorbic acid has been widely used as a reduction reagent in the synthesis of metal nanostructures and the sodium citrate has similar characteristics.<sup>22</sup> The roles of the

citrate ions at the growth process of ZnO nanorods is the selective adsorption of ions on the [0001] surfaces leading to the inhibition of the crystal growth in the [0001] direction.<sup>20</sup> It resulted in the formation of ZnO nanoplates. Ascorbic acid exhibits similar characteristics to slow down crystal growth in the [0001] orientation and therefore provides a simple approach to control the growth process. In addition, the ascorbic acid and downward growth method can reduce the long growth time from 24 to 2 h and control the stratified structure by varying the concentration.<sup>20</sup>

The density of ZnO nanostructures was significantly decreased with the increase in concentration of ascorbic acid. The ZnO nanostructures also became less aligned. In order to improve the alignment of nanopagodas, aligned ZnO nanorod arrays were used as the ZnO seed layer. With equimolar (10 mM) zinc acetate and HMTA as the reaction solution, aligned nanorods with a smooth top surface were formed, as shown in Figure 2a. The diameters and lengths of the nanorods are 20-80 nm and  $1-2 \mu m$ , respectively. Figure 2b shows a top-view SEM image depicting laminated ZnO nanopagoda arrays grown with equimolar (5 mM) zinc acetate and HMTA as well as 0.1875 M ascorbic acid on the ZnO nanorod layer by the downward growth method. The inset image is a high magnification SEM image exhibiting a layered structure of one of the ZnO nanopagodas. The cross sections of ZnO nanopagodas are of hexagonal shape. A 20° tilt SEM image is shown in Figure 2c. The diameters and lengths of the nanopagoda tips are about the same as those grown on the ZnO seed layer. The progressively slender structure of the ZnO nanopagoda is attributed to the depletion of Zn with reaction time in the downward growth process.<sup>21</sup> In contrast, nanopagodas with a smooth top were grown with the upward growth process. Figure 2d shows a 20° tilt SEM image depicting the flat tops of ZnO nanopagoda arrays. To further exhibit the surface structure of the planar top of nanopagodas, a highmagnification SEM image of two nanopagodas are shown in the inset of Figure 2d. The difference indicates that the downward growth process is more suitable to grow the tapered ZnO nanostructures.<sup>21</sup> In addition, the ZnO nanorod layer can be effectively used to grow aligned ZnO nanopagoda arrays. Figure 2e shows the TEM image of a ZnO nanopagoda (corresponding to those shown in Figure 2b) with a length of 1.1  $\mu$ m and a tip diameter of about 5 nm. The ZnO nanopagoda tip is very narrow and sharp. Figure 2f and the inset shows a HRTEM image taken from part of an individual nanopagoda and the corresponding selected area electron diffraction (SAED) pattern, respectively. Both the TEM image and diffraction pattern indicate that the nanopagoda is single-crystalline and grown in the [0001] direction. The XRD pattern of nanopagoda arrays grown on the ZnO nanorod layer is shown in Figure 2g. A strong and sharp diffraction peak corresponding to the (0002) crystal plane of ZnO indicates that the preferred growth direction of the ZnO nanopagoda arrays is in the [0001] direction.

Figure 3a shows a 20° tilt SEM image depicting the structure of thick-layer nanopagodas grown with 0.125 mM ascorbic acid. The inset is a high magnification SEM image exhibiting a layered structure of one of the thick-layer nanopagodas. Owing to the low concentration of ascorbic acid, the inhibition in the growth of ZnO nanoplates of nanopagoda in the [0001] direction is less pronounced. Figure 3b shows TEM image of a thick-layer nanopagoda (in Figure 3a) with a length of 180 nm and a tip diameter of about 8 nm. The high-resolution TEM image taken from part of an individual thick-layer nanopagoda and the corresponding SAED pattern are shown in Figure 3c and the inset, respectively. Both HRTEM image and diffraction



**Figure 2.** (a) Top-view SEM image of a ZnO nanorod layer grown on Si wafer precoated with ZnO seed film, (b) top-view and (c) 20° tilt-view SEM images of nanopagodas grown on a ZnO nanorod layer by the downward growth method. The inset image in (b) is a high magnification SEM image. (d) 20° tilt-view SEM image of ZnO nanopagodas grown on a ZnO nanorod layer with the upward growth process and the inset is a high magnification SEM image. (e) TEM image of a ZnO nanopagoda in (b). (f) HRTEM image and corresponding SAED pattern confirming the single-crystallinity of the ZnO nanopagoda in (e). (g) XRD pattern of ZnO nanopagoda arrays grown on Si wafer pregrown with ZnO nanorod film.



**Figure 3.** (a) 20° tilt-view SEM image of the thick-layer nanopagodas grown on ZnO nanorod layer; inset image is a high magnification SEM image. (b) TEM image of a thick-layer nanopagoda in (a). (c) HRTEM image and SAED pattern confirming the single-crystallinity of the thick-layer nanopagoda in (b). (d) 20° tilt-view SEM image of thin-layer nanopagodas grown on ZnO nanorod layer. (e) TEM image of a thin-layer nanopagoda in (d). (f) HRTEM image and SAED pattern confirming the single-crystallinity of the thin-layer nanopagoda in (e).

pattern indicate that the layered nanopagoda is single-crystalline and grown in the [0001] direction. Figure 3d shows a 20° tilt SEM image of thin-layer ZnO nanopagoda arrays. The surface structure became relatively rough compared to those grown with a lower concentration of ascorbic acid and quite a few tips became blunt. As a high concentration of ascorbic acid is present in the reaction solution, the crystal growth in the [0001] orientation is severely constrained. Figure 3e shows a TEM image of a thin-layer ZnO nanopagoda (in Figure 3d) with a length of 675 nm and tip diameter of about 8 nm. The thicknesses of layers are about 3–20 nm. The narrowing of the top layers of ZnO nanopagodas is originated from depletion of zinc sources with reaction time. On the other hand, the ascorbic acid was still copiously present to retain the final plate-like nanostructure at the end of the reaction. The high-resolution TEM image taken from the edge of the middle section of a nanopagoda and the corresponding SAED pattern are shown in Figure 3f and its inset, respectively. The HRTEM image



**Figure 4.** Cathodoluminescence spectra of the ZnO nanostructures grown on Si wafer precoated with ZnO seed film. (a) Nanoneedles, (b) thick-layer nanopagodas, (c) nanopagodas, and (d) thin-layer nanopagodas.

provides direct evidence of the presence of an intermediate layer separating the ZnO layers of the nanopagoda. In addition, a surface layer is also seen at the edge of ZnO plate. The bright contrast of the intermediate layer indicates that it is constituted of light elements and hence likely to be an organic layer associated with the ascorbic acid. Since the HRTEM image shows a projective view of the ZnO lattice, it may reveal that the crystal lattice is intact underneath the bright contrast organic. On the other hand, ascorbic acid may also bond to the sides of the ZnO plates where the other less favored polar surface planes emerge and inhibit further expansion of ZnO plates laterally as seen in Figure 3f as well as the schematic shown in Figure S3d, Supporting Information. Both the TEM image and diffraction pattern reveal that the thin-layer nanopagoda is single-crystalline and grown in the [0001] direction. The dimensions of nanopagodas grown on the ZnO seed layer and nanorod layer are listed in Table S1, Supporting Information. It is significant that the presence of ascorbic acid not only influences the growth morphology of ZnO but also efficiently decreases the total growth time to 2 h.

Cathodoluminescence is a useful technique for characterizing the optical properties of nanostructures. Since CL uses an electron beam for excitation, it is feasible to excite only a single or a small group of nanostructures. All the CL spectra were taken at room temperature. In order to avoid the interference of thick ZnO nanorod layer on the optical emission properties, only ZnO nanostructures grown on the ZnO seed layer were measured herein. Figure 4 shows CL spectra for nanoneedles and various kinds of nanopagodas. For nanoneedles and thicklayer nanopagodas, strong UV emission occurs at about 377 nm (3.29 eV), which comes from recombination of exciton and almost no emission from defects. The optical properties demonstrate that ascorbic acid is a useful reagent to prepare ZnO nanostructures with superb UV emission and almost no green emission properties relative to the ZnO nanotower bundles in the previous reports.<sup>23</sup> For ZnO nanopagodas, a blue shift to 367 nm (3.38 eV) UV emission was observed. In comparison with the CL measurements from thick-layer nanopagodas with relatively blunt tip widths of about 8-50 nm, the nanopagodas with the narrow tip widths of about 3-30 nm (the average width and length are less than 20 nm and about 100 nm, respectively) exhibit a 10 nm (90 meV) shift in the emission peak. The blue shift is attributed to the quantum confinement effect arising from the reduced size of the bottom plates and tips. In the CL emission spectra, the energy shift of nanorods with diameters far beyond the quantum confinement regime is ascribed to the surface effect due to the increased surface-to-volume ratio.<sup>24</sup>





**Figure 5.** SEM images of the ZnO nanopagoda arrays grown on a fourinch silicon wafer at different locations, magnifications, and tilt angles (0 or  $20^{\circ}$ ). At the center is a photograph of a grown wafer.

For thin-layer ZnO nanopagodas, a blue shift to 367 nm (3.38 eV) at UV emission and a strong green emission at about 585 nm are evident as seen in Figure 4. This result is consistent with the currently accepted model that the green emission arises from the recombination between holes trapped at the surface defects and electrons trapped at the oxygen vacancy.<sup>21,25</sup> The excessive ascorbic acid may induce the formation of ZnO surface defects and influence the optical emission. The thinlayer ZnO nanopagodas are stacked with 3-25 nm ZnO nanoplates, which also exhibit a quantum confinement effect and lead to a blue shift of UV emission. The blue shifts are most significant compared with many other ZnO nanostructures.14,15,24 The excessive ascorbic acid may induce the formation of ZnO surface defects and influence the optical emission. The enhancement in deep-UV optical properties shall facilitate the applications of nanopagodas for nanoscale lightemitting devices.

The ZnO seed layer has been found to be useful in growing ZnO nanowire or nanorod arrays by the ACG method in the four-inch wafer-scale production.<sup>15,25</sup> Herein, we expand on this synthesis method to produce dense arrays of ZnO nanopagodas by the downward ACG method.<sup>21</sup> SEM images taken from several four-inch samples revealed that the entire wafer can be grown with highly uniform and aligned ZnO nanopagoda arrays, as shown in Figure 5. The ZnO nanorod layer is important for growing aligned ZnO nanopagoda arrays. The ZnO nanorod arrays were grown with equimolar (50 mM) zinc nitrate and HMTA by the downward growth method with a growth time of 3 h. The high concentration of ZnO nanorod arrays can provide better surface coverage and enhance the growth of more uniform ZnO nanopagoda arrays on the silicon wafer. The growth time can be used to control the thickness of ZnO nanorods, which was found to influence the growth of aligned ZnO nanopagodas. For ZnO nanorods produced in a short time, the lengths of nanorods were not very uniform. On the other hand, sufficient reaction time led to uniformly grown nanorods, which are conductive to large-scale production. The best condition to grow ZnO nanopagoda arrays in large scale was found to be from a reaction solution with equimolar (5 mM) zinc nitrate and HMTA and the low concentration of ascorbic acid (0.1875 mM). In addition, a large reaction chamber, copious reaction solution, and long reaction time were needed to grow aligned and regular ZnO nanopagodas in large scale.



**Figure 6.** The 20° tilt-view SEM image of nanopagodas grown with (a) 2.5, (b) 5, (c) 7.5, and (d) 10 mM zinc precursor and the same ratio of ascorbic acid grown on ZnO nanorod layer. Inset in (d) is a high magnification SEM image. (f) The schematic illustrating the variation of apex angles of ZnO nanopagodas with the concentration of zinc precursor in the reaction solution.

The variation of concentration of Zn precursor was found to affect the apex angles of the nanopagodas. Figure 6a shows a 20° tilt SEM image depicting the ZnO nanopagodas with small diameters and apex angles. The diameters and the apex angles of the thick-layer nanopagodas tips are 8-30 nm and  $0-9^{\circ}$ , respectively. The long and narrow ZnO nanopagodas were grown from equimolar (2.5 mM) zinc nitrate, HMTA, and a low concentration of ascorbic acid (0.09375 mM) reaction solution. The morphology was similar to nanopagodas with wirelike tips. Appropriate amounts of equimolar (5 mM) zinc nitrate, HMTA, and ascorbic acid (0.1875 mM) led to the growth of ZnO nanopagodas with sharp tips, as shown in Figure 6b. The diameters and apex angles of the nanopagoda tips are 3-16nm and  $3-15^{\circ}$ , respectively. Figure 6c shows 20° tilt SEM image of ZnO nanopagodas grown from equimolar (7.5 mM) zinc nitrate, HMTA, and (0.28125 mM) ascorbic acid reaction solution. The diameters and apex angles of the nanopagoda tips are 5-25 nm and 15-35°, respectively. The apex angles of ZnO nanopagodas are progressively increasing with the concentration of precursor. On the other hand, the lengths of ZnO nanopagodas varied with reverse tendency. Figure 6d shows a 20° tilt SEM image of ZnO nanopagodas grown from equimolar (10 mM) zinc nitrate, HMTA, and (0.375 mM) ascorbic acid reaction solution. The inset is a high magnification SEM image depicting the similar morphology of a nanopagoda. The heights of ZnO nanopagodas have evidently decreased relative to the low concentration condition. Figure 6e shows schematic diagrams illustrating the variation in apex angles with the concentration of zinc precursor and the same ratio of ascorbic acid in the reaction solution.

Both zinc precursor (zinc nitrate and HMTA) and ascorbic acid can alter the apex angles of the ZnO nanopagodas. The lamination of ZnO nanopagodas was adjusted by the concentration of ascorbic acid with the concentration of zinc precursor fixed at 5 mM. The variation of apex angles is depicted in a plot in Figure S1a, Supporting Information. The apex angles of nanopagodas varied from about 10° to 20°. On the other hand, varying the concentration of Zn precursor led to significant changes in apex angles. The four kinds of nanopagodas possess apex angles of  $0-9^{\circ}$ ,  $3-15^{\circ}$ ,  $15-35^{\circ}$ , and  $26-66^{\circ}$ . A plot depicting the relationship between apex angle of nanopagodas and concentration of Zn precursor is shown in Figure S1b, Supporting Information. For a high concentration zinc precursor condition, ZnO nanopagoda arrays did not have enough interspace to grow uniform structure.

The ZnO nanopagodas formed with 5 mM zinc precursor in the reaction solution possess the narrowest and longest tip. In addition, their density is the highest. The length and density tend to decrease with the zinc precursor concentration. With increasing concentration, the nanopagodas were grown to bigger sizes. In the growth with 2.5 mM zinc precursor, both the lengths and density of nanopagodas were decreased owing to the low nucleation rate and rapid depletion of Zn sources with low concentration of Zn precursor.

Microrods with widths of  $1-2 \ \mu m$  were obtained with a concentration of 0.1 M zinc nitrate/HMTA. It was reported that nanorods of about 100–200 nm and 10–20 nm in width can be grown with 0.01 and 0.001 M solutions, respectively.<sup>13</sup> The concentration of zinc nitrate and HMTA can effectively control the sizes of ZnO nanorods. HMTA plays an important role in growing ZnO nanostructures and have been extensively discussed in previous reports.<sup>13,26</sup> Herein, HMTA acts as a pH buffer by slowly decomposing to provide a gradual and controlled supply of ammonia, which can form ammonium hydroxide as well as complex zinc(II) to form Zn(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>. The dehydration of zinc hydroxide intermediates control the growth of ZnO and the slow release of hydroxide may have a profound effect on the kinetics of the reaction.<sup>26</sup>

One-dimensional ZnO nanostructures often possess superb field emission properties because of their favorable geometry.<sup>27</sup> The influences of apex angles of nanopagoda arrays on the field emission properties have been investigated. To minimize the influence of substrate on field emission properties, a thin ZnO nanorod layer was used to grow the nanopagodas with different apex angles. The thickness and uniformity of ZnO nanorod layer can be controlled by the reaction time. Nanorod layers with different thicknesses were grown from 50 mM zinc nitrate and HMTA for 15 or 30 min on precoated seed layer film (Figure S2a-d, Supporting Information). For 15 min growth, the nanorods were not uniform, which led to the poor alignment of nanopagoda arrays as shown in Figure S2e, Supporting Information. For 30 min growth, the nanorod layer was more uniform. As seen in the Figure S2d, Supporting Information, the thickness is about 280 nm. The nanopagoda arrays are more aligned as shown in Figure S2f, Supporting Information.

The measured field emission current density as a function of the electric field is shown in Figure 7a. Turn-on electric fields were obtained at an emission current density of 0.1  $\mu$ A/cm<sup>2</sup>. The turn-on fields for ZnO nanopagodas with different apex angles were found to be 1.44 (2.5 mM), 1.25 (5 mM), 1.34 (7.5 mM), and 1.51 (10 mM) V/ $\mu$ m. For nanopagodas with the smallest tips at the emission current density of 1 mA/cm<sup>2</sup>, the threshold field is 1.97 V/ $\mu$ m.

The Fowler-Nordheim (FN) plot was used to obtain the field enhancement factors of ZnO nanopagodas, as shown in Figure 7b. Fitting the measured data with the following relationship:

$$\ln(J/E^2) = (-B\varphi^{3/2}/\beta)(1/E) + \ln(A\beta^2/\varphi)$$
(1)



Figure 7. (a) Field emission current density-applied electric field (J-E) characteristics of nanopagodas grown with different concentrations of zinc precursor on the thin nanorod film. (b) Corresponding F-N plots.



Figure 8. SEM images of ZnO nanopagodas grown with different periods of time. (a) 0, (b) 30, (c) 50, (d) 70, (e) 90, and (f) 120 min.

where J is the current density, E is the applied electric field, and  $\varphi$  is the work function. A and B are constants, corresponding to 1.54  $\times$  10<sup>-6</sup> A eV V<sup>-2</sup> and 6.83  $\times$  10<sup>3</sup> V eV<sup>-3/2</sup>  $\mu$ m<sup>-1</sup>, respectively. By determining the slopes of the  $\ln(J/E^2)$  vs 1/E plot using the work function value of ZnO (5.3 eV), the fieldenhancement factors  $\beta$  have been determined to be in the range of about 3000-4000 and listed in Table S2, Supporting Information. In most cases, the local field will be amplified by the factor  $\beta$ , which is accordingly termed the field amplification factor.  $\beta$  is determined solely by the geometrical shape of the emitter.<sup>28</sup> Electric field shielding which occurs between closely packed nanofibers in the dense forest lowers the effective field enhancement factor of the high aspect ratio nanofibers.<sup>29</sup> The ZnO nanopagoda arrays prepared with 5 mM have a low turnon field and high field-enhancement factor  $\beta$ . Tunneling electrons through the surface are directly proportional to the size of tips as discharge spots. The aligned ZnO nanopagoda arrays exhibit high crystalline quality and sharp tips with nanosized surfaces, resulting in the highest field enhancement factor of about 4190. In addition, the detrimental antenna effects are expected to be insignificant since the nanopagodas are of moderate density. For nanopagodas prepared with 2.5 mM Zn precursor, the tips were relatively blunt. The field enhancement factor is about 2987. For nanopagodas prepared with 7.5 mM and 10 mM Zn precursor, the detrimental antenna effects are expected to be relatively severe. Compared to ZnO nanowires, the turn-on and threshold electric fields for ZnO nanopagodas prepared under the appropriate conditions are considerably lower, which shall be advantageous in applications as field emitters.<sup>27</sup>

Figure 8a shows a top-view SEM image depicting the hexagonal and smooth top of ZnO nanorods. The ZnO nanorod arrays were grown from equimolar (50 mM) zinc nitrate and HMTA for 3 h by the downward growth method. The diameters and lengths of the nanorods are 50-150 nm and  $1-2 \mu m$ , respectively. The samples were used as the substrates to grow ZnO nanopagodas. Figures 8b-f show top-view SEM images of samples grown for 30, 50, 70, 90, and 120 min, respectively. Initially, ZnO nanocrystals were deposited on the surface of ZnO nanorods, as shown in Figure 8b. The surface of ZnO nanorods was then completely covered with ZnO nanoplates, as shown in Figure 8c. The ZnO nanoplates were stacked to form laminated structures with rough surfaces. With increasing reaction time, the laminated structures became more prominent, with smooth surfaces and sharp tips, as shown in Figure 8d-f. It is apparent that ZnO nanopagodas were gradually stacked by ZnO nanoplates and the surface of ZnO nanoplates became smoother. Well-aligned ZnO nanoneedle arrays were produced from epitaxial growth on (0001)-oriented seed laver by the downward ACG method.<sup>21</sup> For laminated nanopagodas, the inhibition of growth in the [0001] direction by ascorbic acid nonuniformly resulted in a less well aligned structure.

The growth of ZnO nanopagodas can be understood from the inhibited growth on a polar surface. The Wurtzite-structured ZnO crystal can be described schematically as a number of alternating plates composed of tetrahedral coordinated  $O^{2-}$  and Zn<sup>2+</sup> ions and stacked alternatively along the *c*-axis (Figure S3a, Controlled Growth of ZnO Nanopagoda Arrays

Supporting Information).<sup>7</sup> The polar surface of the [0001] plane can be terminated with the top surfaces of positively charged [0001]-Zn and the bottom surfaces of negatively charged [0001]-O, respectively. One-dimensional ZnO nanostructures are easily grown along the c axis of the Wurtzite crystal, which has a hexagonal structure with six nonpolar  $\{10\overline{1}0\}$  prismatic capped by polar oxygen [0001] and zinc [0001] basal surfaces (Figure S3b, Supporting Information). Figure S3c, Supporting Information shows a structure model of L-ascorbic acid. The pentagon has the same plane with two hydroxyls (O-H) and carbon-oxygen double bond (C=O). This bottom plane structure has four lone paired electrons on the four oxygen atoms. These lone paired electrons were easily bonded on the polar surface of positively charged [0001]-Zn by the electrostatic force. In addition, direct evidence of an intermediate organic layer, possibly ascorbic acid, at the polar surface and side (edge) surface was obtained in the atomic resolution TEM image, shown in Figure 3f, of the sample prepared with a high concentration of ascorbic acid. As a result, stepwise structures (nanopagodas) were grown in the downward ACG method. The mechanism is illustrated in Supporting Information, Figure S3d.

## Conclusions

Vertically aligned ZnO nanopagodas have been synthesized on the previously grown aligned ZnO nanorods on Si wafer using a downward ACG method. The tight control in alignment, narrowing of tips, degrees of lamination, and apex angles of nanopagodas are achieved by utilizing the substrate with aligned ZnO nanorods, downward ACG method, and variation in ascorbic acid and change in concentration of Zn precursor in the growth solution, respectively. Low turn-on and threshold fields indicate that narrow and sharp tips of nanopagodas are promising for the application in field emission microelectronic devices. The polar surface concept was invoked to understand the growth mechanism of ZnO nanopagodas. The ZnO nanopagodas exhibit a significant blue shift at UV emission and almost no green emission attributed to singly ionized oxygen vacancies. The enhancement in deep-UV optical properties shall be advantageous in applications for nanoscale light-emitting devices. The appropriate substrates and reaction conditions enhance the growth of ZnO nanopagoda arrays with wafer-scale production. The large-scale ZnO nanopagoda arrays shall be very useful in fabricating novel devices, such as field emitters and ultraviolet lasers.

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**Supporting Information Available:** This information is available free of charge via the Internet at http://pubs.acs.org.

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