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Experimental and computational insights in the growth of gallium-doped zinc oxide nanostructures with superior field emission properties
Experimental and computational insights in the growth of gallium-doped zinc oxide nanostructures with superior field emission properties

Hsien-Ming Chiu, Hsin-Jung Tsai, Wen-Kuang Hsu and Jenn-Ming Wu*

Well-aligned, single-crystalline Ga-doped zinc oxide nanopagoda arrays were fabricated on silicon substrates via a metal–organic chemical vapor deposition method. Gallium atoms played a crucial role in transforming the lateral facets of nanorods from (1100) to two sets of facets: ((1121), (1122)) and ((2201), (1101)), which eventually led to a pagoda shape. Based on computational simulation results, gallium lowers the surface energies of the ((1121), (1122)) and ((2201), (1101)) planes but increases that of the (1100) plane. We proposed a new growth model, which involves the change of surface energy calculated by computational simulation due to Ga doping, to interpret why the smooth (1100) planes of nanorods transform to corrugated ((1121), (1122)) and ((2201), (1101)) planes of nanopagodas. The nanopagodas not only possess excellent crystal quality but also exhibit remarkable field emission properties. Field emitters made of Ga-doped ZnO nanopagodas had a low turn-on field due to the decrease of work function and the increase of conductivity caused by Ga; simultaneously, the interesting pagoda shape enhanced significantly the field emission β values by 18 times.

1 Introduction

One-dimensional (1D) nanostructures such as wires, rods, tubes, rings, belts, and needles, are fascinating materials in fabricating electronic, optical, optoelectronic, electrochemical, and electromechanical devices due to their unique properties such as high aspect ratio and high surface area.1 1D semiconducting materials can function as building blocks for interconnects of transistors, junctions between metals and semiconductors, and the tips of emitters.2 Zinc oxide (ZnO), a II–VI semiconductor, which possesses a direct wide energy gap of 3.37 eV and a large exciton binding energy of 60 meV,3 has recently attracted global interest in applications such as light-emitting diodes,4,5 laser diodes,6,7 solar cells,8 field effect transistors,8 and field emission displays.9,10

Field emission (FE), also known as Fowler–Nordheim tunneling, is a form of quantum tunneling in which electrons pass from an emitting material to the anode through a barrier (vacuum) in the presence of a high electric field.11 In addition to the remarkable progress of carbon nanotubes, the inorganic semiconductor ZnO nanostructures are potential materials in FE applications. The FE properties strongly depend on factors such as work function, emission area, crystal quality, electrical conductivity, geometry shape, and density of the emitter materials. Ga-doped ZnO (GZO) has potential for improving the FE properties because gallium increases the electrical conductivity and lowers the work function of ZnO. However, the effect of Ga doping on the crystal quality, morphology, geometry shape, density, and FE properties of 1D ZnO nanostructures has seldom been studied.12–14

1D ZnO nanostructures can be fabricated by diverse range of processes such as template-assisted synthesis,15 chemical vapor deposition (CVD),4,8,16–18 atomic layer deposition (ALD),5 hydrothermal,18,20–22 and metal–organic chemical vapor deposition (MOCVD).21,22 Among these fabrication processes, MOCVD has several advantages including fine control of the partial pressures of individual reactants and dopants as well as a large area of uniformity. These advantages facilitate reproducible and controlled synthesis of high quality 1D ZnO nanostructures.23

In this work, the effect of Ga doping on the growth of 1D ZnO nanostructures was investigated. The variables investigated include the growth temperature, the Ga/Zn molar ratio of precursor, and the growth time. The morphology of the GZO nanostructures was found to exhibit a nanopagoda (NPG) shape, which was quite different from the usually obtained nanowires (NWs) or nanorods. The GZO nanostructures possessed a nanorod shape as usually observed in the early stage of growth; however, it developed into a pagoda shape in later stages. There were some reports on NPG shape nanostructures. Chang et al. reported that the ascorbic acid additive in wet chemical solutions adsorbed onto (0001) plane of ZnO, forming laminated ZnO NPGs.24 Song et al. reported that the Zn adatoms diffused or desorbed from the GaN facets under O-rich condition, leading to...
the formation of corrugated ZnO nanorods. Wang et al. reported the cubic ZnMgO/hexagonal ZnMgO interlayer/ZnO nucleating layer heterostructure NPGs under the presence of MgO. After deliberating these reported models which could all be classified as adsorbing chemical species onto either Zn-polar (0001) or O-polar (0001) planes, we found that this model is not suitable for our work because Ga is uniformly substituted for Zn atom in the entire NPG under doping condition. Therefore, we proposed a new growth model, which is based on the change of surface energy as calculated by computer simulation due to Ga doping, to interpret the transformation from the lateral planes (1100) of smooth nanorods to two sets of facets: (1121), (1122) and (2201), (1101) of corrugated NPGs. Finally, we report the remarkable FE properties of the GZO NPGs under various growth conditions.

2 Experimental

2.1 Deposition of GZO seed layer

The GZO seed layer was deposited on Si (100) substrates by radio frequency (RF) magnetron sputtering at room temperature using a 1% GZO target. The sputtering power was kept at 45 W; working pressure was 10 mTorr; sputtering gas was 100% Ar; and the deposition time was 1 h. The seed layer was 200 nm thick with a wurzite (0002) preferred orientation measured by SEM and XRD. The Hall properties of the GZO seed layer were measured. Its carrier concentration is 7.86 × 10^{15} cm^{-3}, mobility 50.04 cm^2 V^{-1} s^{-1}, and resistivity 1.59 × 10^{-3} Ω cm. The GZO seed layer is excellent to serve as back electrodes for further optoelectronic devices measurements and applications.

2.2 Growth of GZO nanostructures

The GZO nanostructure arrays were then fabricated on the pre-deposited GZO seed layer via MOCVD. Zinc acetylacetonate hydrate [Zn(acac)_2·xH_2O] (Aldrich, powder), oxygen gas, and gallium acetylacetonate [Ga(acac)_3] (Aldrich, 99.99%) were used as the Zn, O, and Ga doping sources. Nitrogen was introduced as the precursor carrier gas. Zn(acac)_2·xH_2O and Ga(acac)_3 powders were placed together in an outer glass vessel. The whole fabrication process was kept at a reaction horizontal quartz furnace from 450 to 850 °C; and the outer vessel was heated to 135 °C. The Zn(acac)_2·xH_2O and Ga(acac)_3 started to evaporate after their temperatures were higher than about 110 and 130 °C, respectively. The O_2 and N_2 flow rates were kept at 300 and 500 sccm respectively; working pressure was maintained at 3–4 mTorr by a mechanical pump; and the reaction time was 5 min to 1 h. The effect of Ga contents was investigated by varying the Ga/Zn molar ratios in the precursor as 0.041, 0.102, 0.410, 0.614, and 0.819.

2.3 Characterization of GZO nanostructures

The cross-section and surface morphologies of as-prepared nanostructures were examined by a field emission scanning electron microscope with an accelerating voltage of 15 kV (FESEM, JEOL6500). The phases of GZO NPGs arrays were analyzed by either grazing incident X-ray diffraction (GIXRD, PANalytical X’Pert Pro (MRD)) or gonioc scan X-ray diffraction (XRD, Shimadzu XRD6000) techniques with the Cu Kα radiation. The chemical composition of GZO NPGs was analyzed by Auger electron microscope with an accelerating voltage of 10 kV (AES, ULVAC-PHI7000). The GZO NPGs were observed by a high resolution scanning transmission electron microscope (HR-STEM, JEM2100F) or by an analytical transmission electron microscope (AEM, JEM2010) at an accelerating voltage of 200 kV. The cross-section TEM samples were prepared with a focused ion beam (FIB, FEI Nova200) instrument. Low-temperature cathodoluminescence (CL) spectroscopy was performed at 10 K with a field emission scanning electron microscope (JSM7001F).

2.4 Electrical measurements of GZO and ZnO nanostructures

To determine the electrical conductivities of GZO and ZnO nanostructures, three-terminal single nanowire field effect transistor devices were fabricated as followed. As-grown GZO NPGs (Ga/Zn precursor ratio = 0.410) and pure ZnO NWs (both were grown at 750 °C for 1 h) were transferred onto heavily doped p+ Si substrates with a 300 nm thick SiO_2 film on the top. The heavily doped p+ Si substrate can serve as the back-gate electrode for further device characterization in the three terminal single nanowire field effect transistors. The source and drain Pt electrodes were subsequently made at the two ends of a single GZO NPG as well as a single ZnO NW with the aid of a FIB apparatus. The I–V characteristics of the three-terminal single nanowire field effect transistor devices were performed by a semiconductor analyzer (Agilent B1500A) under ambient condition at room temperature. Field emission properties of GZO NPGs arrays were measured by an electrometer in a vacuum chamber (<5 × 10^{-6} Torr) at room temperature (FE, Keithly-2410). The distance between the anode and the emitting surface was in a range about 20–70 μm and the diameter of anode was 1 mm.

2.5 Computational simulation

The surface energies of GZO were simulated according to an ab initio method with the CASTEP plane-wave code. First, a 2 × 2 × 2 ZnO wurzite supercell was built. The lattice parameters were set as a = 6.499 Å, b = 6.499 Å, c = 10.411 Å, α = 90°, β = 90°, γ = 120°. Second, representative (1120), (1100), (1121), (1122), (1101), and (2201) plane slabs were created in vacuum, in which some Zn atoms were replaced by Ga (e.g. two Zn atoms were replaced by Ga atoms in order to have a doping contents equivalent to 4.2%). Third, the density functional theory (DFT) was treated with exchange-correlation and Perdew-Ultrasoft pseudo-potentials; the self-consistent field (SCF) tolerance threshold was set as 10^{-6} eV at^{-1} for the structural convergence and 0.05 Å^{-1} for the Monkhorst-Pack k-point grid separation, respectively.

3 Results and discussion

3.1 The effects of the growth temperature on GZO nanostructures

There were no apparent 1D nanostructures observed at 450 °C and 550 °C. Fig. 1 shows the SEM images of GZO nanos-
structures growing at 650, 750, and 850 °C for 1 h with a Ga/Zn precursor ratio = 0.410. Fig. 1(a), (c) and (e) are top views of GZO nanostructures, while Fig. 1(b), (d) and (f) are tilt views. The insets in Fig. 1(a), (c) and (e) are the corresponding cross sections. The GZO nanostructures grown at 650 °C are nanorods possessing an interesting pagoda shape. The lengths of NPGs were not uniform, indicating that NPGs started to grow at different times. It implies that nucleation of NPGs continued during the growth period.

When the growth temperature increased to 750 °C, the 1D GZO NPGs possessed longer pagoda sections than those growing at 650 °C. In addition, some NPGs were observed to have hexagonal pagoda sections shifting with an angle of about 30° among adjacent sections (as shown by the arrow). From the cross section view, the lengths of NPGs were much more uniform compared to those growing at 650 °C, implying that the nucleation of NPGs occurred at similar times. It indicates that the nucleation rates of NPGs are relatively high so that most nucleation sites were exhausted in a short time.

The average lengths of NPGs are longer than that of NPGs growing at 650 °C.

When the temperature further increased to 850 °C, the densities of the GZO NPGs dramatically decreased, while the lengths and the diameters increased. The angular shifting between hexagonal pagoda sections of the GZO NPGs became more noticeable. The sections of NPGs even became distinct and were not uniform. The sharply reduced densities of GZO NPGs show that the nucleation rates were low. Since nucleation continued during the growth period, NPGs started to grow at different times. Consequently the lengths of NPGs differed significantly.

According to the SEM observation, the nucleation of GZO NPGs exhibited a maximum near 750 °C, while the growth rate continued to increase with temperature within 650–850 °C. Temperature is a very important factor which affects the morphologies of the GZO nanostructures.

Fig. 2(a) shows the gonio scan XRD patterns of GZO NPGs obtained from Fig. 1. All XRD patterns exhibit a single sharp ZnO (0002) diffraction peak. It shows that GZO NPGs grew
essentially perpendicular to seed layers. The FWHMs of GZO NPGs grown at 650, 750, and 850 °C are 0.35, 0.24, and 0.25°, respectively, indicating that the GZO NPGs fabricated at higher temperatures possessed better crystalline quality. In addition, the integrated intensity of the ZnO (0002) diffraction peak increased with the growth temperature of the GZO NPGs (Fig. 2(b)), which demonstrates that the total amount as well as the crystalline quality of GZO NPGs increases with temperature. Fig. 2(b) also demonstrates that the diffraction angle of the (0002) peak shifts to higher angles, exhibiting the decrease of lattice parameter $c$ with the growth temperature. It is attributed to the smaller Ga$^{3+}$ ions (47 pm) substitution for larger Zn$^{2+}$ ions (60 pm). The observation suggests that the doped Ga concentration increases with the growth temperature under the same Ga/Zn precursor ratio.

3.2 The effects of the Ga/Zn molar ratios on GZO nanostructures

Since the doping of Ga is an important factor affecting the shape of the GZO nanostructures, it is beneficial to study the effect of the Ga concentration on the growth of GZO nanostructures. Fig. 3 shows the SEM images of the GZO nanostructures growing at 750 °C for 1 h with different Ga/Zn precursor ratios. The SEM images show that the pagoda shape of GZO nanostructures started to develop at a Ga/Zn precursor ratio higher than 0.102. When Ga/Zn precursor ratio is lower than this value, the shape of GZO nanostructures is the same as pure ZnO nanostructures; however, when the Ga/Zn precursor ratio is higher than this value, the shape of the pagoda does not change significantly. It suggests that there is a critical doping concentration for the pagoda shape to develop. Some geometry features of GZO nanostructures were calculated from SEM images and summarized in Table 1. No significant change was found in the base diameters with the Ga/Zn precursor ratios, while the densities of GZO nanostructures increased slightly with the Ga doping. The tip widths and the apex angles of GZO nanostructures almost remained unchanged with the Ga doping, indicating that the radial growth rate of GZO nanostructures was not affected by the Ga doping. In contrast, the axial growth rate was influenced by the Ga doping as was observed and revealed below. The average lengths of GZO nanostructures demonstrated that the growth rate of GZO nanostructures decreased substantially with the increasing Ga concentration. The Ga contents of the GZO nanostructures were determined by Auger electron spectroscopy and were listed in Table 1. Fig. 3(g) shows a typical Auger electron spectrum (AES) of one GZO nanostructure growing at 750 °C for 1 h. The signals at 516, 995, and 1068 eV are assigned to Auger transition of O KL2L2,ZnL2M4,5, and Ga L3M4,5M4,5, respectively. The incorporated Ga contents in the GZO nanostructures increases abruptly initially, and then increases linearly with the Ga/Zn precursor ratios. It indicates that the incorporation of Ga in the GZO nanostructures becomes harder at higher Ga doping.

To emphasize more on the top GZO nanostructures rather than the bottom seed layer and substrates, we applied GIXRD to reveal the crystal structures of the GZO nanostructures. Fig. 4(a) shows the GIXRD patterns obtained from Fig. 3 performed under a 0.5° grazing angle. All GIXRD patterns show an intensive, sharp (0002) diffraction peak of ZnO at ca. 34.5° along with several very weak diffractions. It corresponds to the almost vertical growth of (0002) GZO nanostructures with only slight tilt. The peak intensity decreased noticeably with the Ga doping. The (0002) peak was plotted versus the Ga/Zn precursor ratios in Fig. 4(b), demonstrating the decrease of the integrated intensity with the increase of the Ga/Zn precursor ratios. Since the integrated intensity and the average lengths of the GZO
nanostructures essentially follow the same trend as shown in the figure, the change of the integrated intensity should be attributed to the change of the axial growth rate of GZO nanostructures caused by Ga doping.

In addition, calculated peak positions of the (0002) peak were also plotted in Fig. 4(c), exhibiting that the diffraction peak positions increased with the Ga contents. The shifting of diffraction peak to higher angle is attributed to the smaller Ga\(^{3+}\) ions substitution for larger Zn\(^{2+}\) ions in ZnO crystals as was described in Fig. 2. The shifting of the peak positions essentially follows the trend of the determined Ga contents of the GZO nanostructures as shown in Fig. 4(c). The Bragg angles between 

### Table 1: Characteristics of GZO NPGs nanostructures growing at 750 °C for 1 h with various Ga/Zn precursor ratios

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<td>10–30</td>
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<td>103</td>
<td>25–60</td>
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\(^{a}\) Quantification by Auger electron spectrum (AES).

3.3 The time evolution and spatial epitaxial orientation of the GZO nanostructures

To understand how GZO NPGs developed, SEM was employed to investigate the evolution of the morphologies of GZO NPGs during growth. Fig. 5 shows the SEM images of the GZO NPGs with a Ga/Zn precursor ratio = 0.410 growing at 750 °C for various periods of time. For better observation of the progression of the morphologies, both the tilt (right) and the top (left) views with corresponding illustrative schematic diagrams (inset) are shown in Fig. 5. Fig. 5(a) shows the image of GZO nanostructures growing for 5 min, indicating that the morphology possesses a rod shape with smooth surface. Later, the smooth lateral surface will be identified as the \{1100\} facet by TEM. When the growth time increased to 10 min, the morphology changed from a rod to a cone shape with a narrower top as shown in Fig. 5(b). The angle between the lateral surface and the central axis of the cone-like GZO nanostructures is about 15.6°, which is close to the ideal value 15.12° between \{1100\} and \{2201\} facets. When the growth time increased to 15 min, the GZO nanostructures developed to a pagoda shape. When the growth time increased to 30 min, some GZO NPGs (indicated by arrows) exhibited two hexagonal sections with an angle of about 29.4° between them. When the growth time increased over 30 min, the morphology remained nearly unchanged. To further examine the morphology, TEM was employed to determine the characteristic facets of the GZO NPGs.

Fig. 6 shows the TEM images (left) and high resolution TEM images (right) of the GZO nanostructures growing at 750 °C with a Ga/Zn precursor ratio = 0.410 for 5 min, 10 min, and 1 h (same samples as those shown in Fig. 5) with corresponding selected area electron diffraction (SAED) patterns in the insets. Fig. 6(a) shows the TEM image of an isolated GZO nanorod growing for 5 min. The SAED pattern which has a [1120] zone axis demonstrates that the GZO nanorod is single-crystalline. After identifying the SAED pattern directions, the lateral exposed facet is determined as \{1100\} similar to what was reported previously. The TEM image shows that the surface of the GZO nanorod seems smooth. However, the HR-TEM image exhibits that the lateral surface is not smooth if the region marked by a white rectangle is magnified. The lateral surface possesses corrugations similar to a pagoda shape. The directions of the corrugated facets can be determined by the angles between the basal and the facets. The GZO nanorod is c-axis oriented, the basal facet (red line) of the nanorod can be identified as the O-polar (0002) facet. The angle between one exposed facet (blue line) and the basal (0002) facet is about 75°. The angle between the \{2201\} and (0002) facets has a theoretical value of 74.88°. Therefore, the facet can be indexed as \{2201\}. Similarly, the angles between the other exposed facet (green line) with the basal (0002) facet and with the \{2201\} facet are 117° and 136°, respectively. The theoretical angles between \{1101\} and the corresponding planes are...
118.39° and 136.49°, respectively. The exposed facet (green line) can be indexed as {1101}.

Fig. 6(b) shows the TEM image of an individual GZO nanorod growing for 10 min. The inset is the corresponding SAED patterns with a [1100] zone axis. The lateral surface of the GZO nanorod exhibits a gradually tapered shape. The lateral exposed facet can be indexed as {1121} and {1122}. The HR-TEM image taken from the region marked by the white rectangle demonstrates that the lateral surface of the GZO nanorod becomes more corrugated and rougher. The directions of the exposed facets can be determined either from the angles between the basal and the exposed facets or from the electron diffraction spots. The two exposed facets have developed to long {1121} and short {1122} facets. The angle between the long exposed {1121} facet (yellow line) and the basal (0002) facet is about 73°, which is very close to the theoretical 72.67°. Similarly, the angles between the short exposed {1122} facet (pink line) with the basal (0002) facet and with the {1121} facet are measured to be 122° and 131°, respectively; they are very close to the theoretical angles 121.96° and 130.71°, respectively.

The exposed facets identified in this 10 min sample are {1121} and {1122} facets. In contrast, the exposed facets indexed for the 5 min sample are {2201} and {1101}. The {1121} facet and the {2201} facet in each set of the exposed facets have an angle of 17.33° and 15.12° with the (0002) axial direction, respectively; they are very close to the measured angle between the lateral surface and the central axis of these cone-like GZO nanorods, about 15.6° as reported in Fig. 5(b). The orientations of these two sets of exposed facets have a 30° shift from each other, which corresponds to the observed 29.4° angle shift between two hexagonal sections mentioned in Fig. 5(d). Based on the observation, the exposed long and short facets of GZO NPGs should contain ({1121}, {1122}) facets as well as ({2201}, {1101}) facets simultaneously.

All samples growing for longer than 30 min show similar characteristics so that only the sample growing for 1 h is shown in Fig. 6(c). The inset in Fig. 6(c) is the corresponding SAED pattern with a [1100] zone axis. The lateral surface exhibits a much more well-defined pagoda-like contour comparing with those short time samples. The lateral exposed facets are also determined as {1121}, {1122}. The HR-TEM image taken from the region marked by the white rectangle exhibits the exposed facets of the NPG more clearly. The lattice spacings of several planes in the HR-TEM image are measured as 0.26, 0.16, and 0.14 nm, which agree well with the values for (0002), (1120), and (1122) crystal planes, respectively.

The spatial relations between GZO NPGs and GZO seed layer are important for revealing the growth behavior. They were investigated by cross-section TEM images with the aid of focused ion spatial beam (FIB) apparatus, the results are shown in Fig. 7. The relations are concluded as below:

- $[1100]_{\text{GZO}, \ NPGs} || [1100]_{\text{GZO}, \ film}$(0002)$_{\text{GZO}, \ NPGs} || (0002)$_{\text{GZO}, \ film}$

and

- $[1100]_{\text{GZO}, \ film} || [110]_{\text{Si}}$(0002)$_{\text{GZO}, \ film} || (0002)$_{\text{Si}}$

The orientation of the GZO thin film is (0002). At the GZO–Si interface, Si (002) is parallel to GZO (0002) with inter-planar spacings of 0.2774 and 0.2668 nm, respectively. The lattice mismatch is only about 3.9%. In contrast, in the directions of GZO [1100] and Si [110], the inter-planar spacings are 0.2874 and 0.3842 nm, respectively. The lattice mismatch is as large as 33.6%. The lattice mismatch of the growth plane (in-plane)
affects the growth more strongly than that along the growth direction (out-of-plane). Therefore, the GZO seed layer not only acts as a platform for the epitaxial GZO NPGs but also as a bottom electrode for further device application.

From the observations of SEM and TEM, the progress of the GZO NPG can be concluded as follows and is shown in Fig. 8: initially, the GZO nanostructures grow to a nanorod shape along the (0002) direction with a \{11\overline{2}0\} type of surface, but the \{1100\} surface possesses fine corrugated facets, containing either \{(11\overline{2}1), \{11\overline{2}2\}\} facets or \{(2201), \{1101\}\} facets. With increasing time, the GZO nanorods become a cone shape with a semi-angle of about 15.6°. The surface of the cone-like nanorods is composed of either \{(11\overline{2}1), \{11\overline{2}2\}\} facets or \{(2201), \{1101\}\} facets. As the growth time progresses, the nanostructures become NPGs with much well-defined and longer hexagonal sections. As the growth time further progresses, the well-defined hexagonal sections possess both \{(11\overline{2}1), \{11\overline{2}2\}\} facets and \{(2201), \{1101\}\} facets.

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Fig. 6 The TEM images (left) and high resolution TEM images (right) of the GZO nanostructures grown at 750 °C with a Ga/Zn precursor ratio = 0.410 for (a) 5 min; (b) 10 min; and (c) 1 h with corresponding selected area electron diffraction (SAED) patterns in the insets.
Based on experimental results, the formation of GZO NPGs using MOCVD was activated by the doping of Ga in ZnO. Since the specific lateral (\{112\}/\{112\}) and/or (\{220\}/\{110\}) planes of the NPGs were transformed from the \{110\} of the nanorods in the later stages of growth, it was speculated that these specific planes possessed lower surface energies due to Ga doping. The surface energies of the \{110\} and \{112\} planes were reported to be lower than those of the (\{112\}/\{112\}) and (\{220\}/\{110\}) planes in pure ZnO materials; however, no surface energies of GZO had been reported previously.29–35 Herein, the influence of Ga doping on surface energies of the corresponding planes was carried out by simulation with a computational DFT protocol.

### 3.4 Computational simulation of surface energies of GZO nanostructures

For the simulation of each surface, we use a slab composed of a multiple unit cells and empty space. The two boundaries of the slab facing empty space are the target surfaces. The (1120) surface plane of the visual 3D wurtzite supercell is shown in Fig. 9(a), in which two Zn atoms are replaced by Ga (equivalent to 4.2% Ga doping). The thickness of the surface box is set at 6.38 Å, the vacuum orientation is along the \(c\)-axial and the thickness is defined as 15 Å. It is sufficiently wide to render negligible the effect of the potential of the opposite surface. The geometries were optimized in both calculations. The surface energy, \(E_s\), can be estimated by using:

\[
E_s = \frac{1}{2} \times (E_{\text{slab}} - E_{\text{bulk}})
\]

where \(E_{\text{slab}}\) is the total energy of the ZnO slab and \(E_{\text{bulk}}\) is the total energy of bulk ZnO composed of the same number of atoms. The visual 2D top view of the other (1100), (1121), (1122), (1101), (2201) slab surfaces are also shown in Fig. 9(b)–(f). The computationally calculated Zn–O and Ga–O bond lengths before and after Ga doping in the relaxation superlattices are listed in Table 2. In the pure ZnO superlattice, Zn atoms have a tetrahedral coordination with a computed Zn–O bond length of 1.992 Å. In the GZO superlattice, the computed Ga–O bond lengths are shortened to a range from 1.775 to 1.961 Å. This is also consistent to the shifting of XRD diffraction angle of the (0002) peak to higher angle when Ga is doped into ZnO.

Table 3 lists the results of computationally calculated surface energies of six crystal planes before and after Ga doping in the ZnO superlattice. We found both terms of \(E_{\text{slab}}\) and \(E_{\text{bulk}}\) increased after the Ga doping. Whereas, the relative difference in these two terms causes the final simulated surface energies of \{1100\} and \{1120\} nonpolar surface planes, which usually appear as lateral surfaces of wurtzite-type ZnO nanostructures, to exhibit an increase of +2.92 and +2.51%, respectively, after 4.2% Ga doping. The increasing surface free
energies of these crystal planes are unfavorable for them to appear during crystal growth in an atmosphere containing Ga. In contrast, the surface energies of the other four oblique polar surface planes \{112\bar{1}\}, \{112\bar{2}\}, \{2\bar{2}01\}, and \{1\bar{1}01\} decrease by 2.50, 2.42, 2.52, and 2.31, respectively, after 4.2% Ga doping. The decreasing surface free energies of these crystal planes are favorable for them to appear during crystal growth in an atmosphere containing Ga. It is reasonable that surface energies of certain planes decrease relative to some other planes by Ga doping. Among these planes, it is worth noticing that the decrease of the surface energy of the \{1\bar{1}01\} planes is very high, at about 32%, which is much higher than the others. One of the possible reasons is due to the much smaller cutting slab surface area 76.79 Å² than the others.

The change in the surface energies of various planes explains the morphology change of the GZO nanostructures from nanorods with smooth lateral surfaces to NPGs with corrugated lateral surfaces.

3.5 Optical and electrical properties of GZO nanostructures

The crystal qualities of ZnO-based nanostructures can be revealed from low temperature (10 K) CL spectra of the pure ZnO NWs and GZO NPGs with a Ga/Zn precursor ratio = 0.410 growing at 750 °C for 1 h, which are shown in Fig. 10(a). A very strong near-band-edge (NBE) peak is observed near 3.344 eV, which is attributed to both free exciton emission and neutral donor bound excitation. The smaller diameter of GZO NPGs would cause a blue-shift of the peak; while the band gap narrowing due to Ga doping in ZnO (with Ga contributing to a shallow donor level) would contribute a red-shift of the NBE peak.23,36,37 In comparison with the pure ZnO NWs, a very small red-shift of about 0.002 eV is observed for the GZO NPGs in the figure, which is probably caused by compensation of these two effects. Further, the broad deep-level emission (DL) peak which normally appears around 2.5 eV is not observed, implying that the GZO NPGs exhibit very good crystal quality without defects like oxygen vacancies and zinc interstitials.

FE measurements were performed to explore the effect of Ga doping on FE properties of ZnO-based nanostructures. Fig. 10(b)–(e) show the emission current density as a function of electric field (J–E) plot and the \(\ln(J/E^2)\) as a function of \(1/E\) plot, respectively. The emission current density (J) produced by a given electric field (E) can be described by the Fowler–Nordheim (F–N) equation:

\[
J = (A\beta^2 E^2/\phi) \exp(-B\phi^2/\beta E) \tag{2}
\]

or

\[
\ln(J/E^2) = \ln(A\beta^2/\phi) - B\phi^2/\beta E \tag{3}
\]

where, \(A = 1.54 \times 10^{-6} \text{ A eV V}^{-2}, B = 6.83 \times 10^3 \text{ eV}^{2/3} \text{ V} \mu\text{m}^{-1}, \phi = \text{work function of material, } \beta = \text{field enhancement factor.}

In Fig. 10(b), the turn-on field, which is defined as the applied field attaining a current density of 0.1 \(\mu\text{A cm}^{-2}\), is determined to be about 0.83 \(\text{V} \mu\text{m}^{-1}\) for pure ZnO NWs, and 0.45, 0.37, and 0.31 \(\text{V} \mu\text{m}^{-1}\) for the 650 °C nanorods, 750 °C NPGs (high density), and 850 °C NPGs (low density) with a Ga/Zn precursor ratio = 0.410, respectively. Ga doping causes a significant decrease of turn-on field. Furthermore, in

**Table 2** Computed zinc–oxygen and gallium–oxygen distances in ZnO wurtzite structure with 4.2% Ga doping

<table>
<thead>
<tr>
<th>Crystal planes</th>
<th>ZnO, Zn–O [Å]</th>
<th>4.2% GZO, Ga–O [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>1.992</td>
<td>1.893</td>
</tr>
<tr>
<td>(110)</td>
<td>1.992</td>
<td>1.808</td>
</tr>
<tr>
<td>(112)</td>
<td>1.992</td>
<td>1.927</td>
</tr>
<tr>
<td>(112)</td>
<td>1.992</td>
<td>1.961</td>
</tr>
<tr>
<td>(200)</td>
<td>1.992</td>
<td>1.775</td>
</tr>
<tr>
<td>(111)</td>
<td>1.992</td>
<td>1.777</td>
</tr>
</tbody>
</table>
Fig. 10(d), the turn-on field is also determined to be about 0.37, 0.39, 0.42, and 0.54, accordingly, for Ga/Zn precursor ratios = 0.041, 0.102, 0.614, and 0.819 growing at 750 °C for 1 h. The turn-on field is insensitive to the contents of Ga doping. Based on calculations from the slopes of the ln(J/E^2) versus 1/E plot at high applied electric field shown in Fig. 10(c), the field enhancement factors \( b \) are calculated to be 304, 319, 1958, and 942, respectively, for pure ZnO NWs and GZO nanostructures with a Ga/Zn precursor ratio = 0.410 growing at 650, 750, 850 °C for 1 h. In Fig. 10(e), the \( b \) values are calculated to be 2126, 5483, 1458, and 1182 for GZO NPGs with Ga/Zn precursor ratios = 0.041, 0.102, 0.614, and 0.819 growing at 750 °C for 1 h. These FE characteristics of each condition were summarized in Table 4. In comparison with pure ZnO NWs, the \( b \) factor of GZO NPGs (Ga/Zn precursor ratio = 0.102, 750 °C) increases by about 18 times. This \( b \) factor of GZO NPGs is better than most of the works reported previously for ZnO nanostructures.\(^2,13,14,20,22,38–43\)

The FE ability strongly depends on various factors: (i) work function, (ii) emission area, (iii) crystal quality, (iv) electrical conductivity, and (v) geometry shape as well as density of emitter materials.\(^38,44\) The emission area and the crystal quality effect can be ruled out because both of pure ZnO NWs and GZO NPGs possess similar nanostructured array area and excellent crystal quality with few defects. The turn-on fields of GZO NPGs are lower than that of the ZnO NWs by about 0.4–0.5 V. It was reported that a 5% doping of Ga lowered the work function of ZnO by about 0.4 eV. Therefore, the lowering of turn-on field caused by Ga doping can be attributed mainly to the decrease of the work function, and partly to the increase of the electrical conductivity.\(^37,44,45\)

The electrical conductivities were calculated from the source-drain current (\( I_{ds} \)) versus drain bias voltage (\( V_{ds} \)) curves under zero gate voltage (\( V_g = 0 \) V) measured from fabricated three terminal single nanowire field effect transistors. The obtained electrical conductivities are 4.049 \( \Omega^{-1} \) cm\(^{-1} \) and 12.658 \( \Omega^{-1} \) cm\(^{-1} \) for single ZnO NW and single GZO NPG, respectively. These values are comparable with previous reports.\(^46\)

### Table 3 Theoretically calculated surface energies of pure ZnO and GZO crystals

<table>
<thead>
<tr>
<th>Crystal planes</th>
<th>Surface area [Å(^2)]</th>
<th>ZnO (this work) [J m(^{-2})]</th>
<th>ZnO(^a) [J m(^{-2})]</th>
<th>4.2% GZO [J m(^{-2})]</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1100)</td>
<td>67.65565</td>
<td>0.617</td>
<td>1.12</td>
<td>0.635</td>
<td>+2.92</td>
</tr>
<tr>
<td>(1120)</td>
<td>117.183</td>
<td>0.835</td>
<td>1.06</td>
<td>0.856</td>
<td>+2.51</td>
</tr>
<tr>
<td>(1121)</td>
<td>122.662</td>
<td>1.187</td>
<td>2.22</td>
<td>1.127</td>
<td>−5.05</td>
</tr>
<tr>
<td>(1122)</td>
<td>138.1379</td>
<td>1.966</td>
<td>2.18</td>
<td>1.882</td>
<td>−4.27</td>
</tr>
<tr>
<td>(2201)</td>
<td>140.1651</td>
<td>1.718</td>
<td>—</td>
<td>1.630</td>
<td>−5.12</td>
</tr>
<tr>
<td>(1101)</td>
<td>76.79</td>
<td>2.132</td>
<td>1.73</td>
<td>1.460</td>
<td>−31.52</td>
</tr>
</tbody>
</table>

\( ^a \) Ref. 30.
GZO NPGs possess much larger $\beta$ values than ZnO NWs. For the GZO NPGs grown at 750 °C with various contents of Ga doping, the $\beta$ values are mostly in the range of 1200–2200 with a maximum (5483) occurring at the Ga/Zn precursor ratio = 0.102. These GZO NPGs possess similar morphologies. However, if we compare the length of NPG data listed in Table 1 with the $\beta$ values, the $\beta$ values appear to increase with the length of the NPGs effectively, except the two with lowest Ga/Zn precursor ratio. It is noted that the apex angle of the NPG which exhibits the highest $\beta$ value (Ga/Zn precursor ratio = 0.102) is the smallest among all. It may imply that the tip shape is an important factor for $\beta$ values: sharper tip reveals higher $\beta$ value. As for GZO NPGs with a constant Ga/Zn precursor ratio = 0.410, the $\beta$ value varies enormously (from 319 to 1958) with the growth temperature; the one grown at 750 °C exhibits a much higher $\beta$ value than the others grown at 650 and 850 °C. From the SEM images shown previously, the GZO NPG grown at 750 °C possesses a much higher density of NPGs and more uniform length than those grown at 650 and 850 °C. Based on these observations, the $\beta$ value is concluded to depend mainly on the geometry shape and density of the GZO nanostructures. Finally, the increase of the turn-on field and the decrease of the $\beta$ value of GZO NPGs with the Ga doping occurred when the Ga/Zn precursor ratio was higher than 0.614 may be due to the Burstein–Moss effect and the screening effect caused at high Ga doping.

### 4 Conclusions

In summary, large area, vertically well-aligned single-crystalline GZO NPGs arrays were grown on GZO seed layer/Si substrate via MOCVD method at various temperatures. The nucleation of GZO NPGs had a maximum at about 750 °C. When the Ga contents were higher than about 3% (Ga/Zn precursor ratio = 0.102), the GZO nanostructures developed a NPG shape.

The evolution of the lateral exposed facets of GZO NPGs was examined using TEM and SEM. The transformation of the lateral exposed facets can be understood through computational simulation. Furthermore, according to the computational simulation, it was concluded that the surface energies of two crystal planes {1100} and {1120} increased by +2.92 and +2.51% while those of the four oblique crystal planes {1121}, {1122}, {2201}, and {1101} decreased by −5.05, −4.27, −5.12, and −31.52% when 4.2 mol% Ga was doped into ZnO. The simulation results explain that doping of Ga helps to form corrugated GZO NPGs with {1121}, {1122}, {2201}, and {1101} planes and suppresses the formation of smooth ZnO NWs with lateral {1100} and {1120} planes.

The CL spectrum of GZO NPGs shows a strong characteristic NBE peak without any DL emission peak. The electrical field emission showed that the turn-on field was very low for GZO NPGs with a Ga/Zn precursor ratio = 0.102 growing at 750 °C for 1 h. Its field enhancement factor ($\beta = 5438$) was enhanced by 18 times in comparison with pure ZnO NWs. These unique GZO NPGs are of potential in applications such as field emitter materials and field emission displays.

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### Notes and references
