

# Synthesis of $\text{In}_2\text{O}_3$ Nanowire-Decorated $\text{Ga}_2\text{O}_3$ Nanobelt Heterostructures and Their Electrical and Field-Emission Properties

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**ABSTRACT** We report on the synthesis of  $\text{In}_2\text{O}_3$  nanowire-decorated  $\text{Ga}_2\text{O}_3$  nanobelt heterostructures via a simple catalyst-free method. A typical heterostructure, where an  $\text{In}_2\text{O}_3$  nanowire forms a sort of a “dorsal fin” on the  $\text{Ga}_2\text{O}_3$  nanobelt, exhibits the T-shaped cross-section. The structure, electrical properties, and field-emission properties of this material are systematically investigated. The heterostructures possess a typical n-type semiconducting behavior with enhanced conductivity. Field-emission measurements show that they have a low turn-on field ( $\sim 1.31 \text{ V}/\mu\text{m}$ ) and a high field-enhancement factor (over 4000). The excellent field-emission characteristics are attributed to their special geometry and good electrical properties. The present  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures are envisaged to be decent field-emitters useful in advanced electronic and optoelectronic nanodevices.

**KEYWORDS:**  $\text{Ga}_2\text{O}_3$  nanobelt ·  $\text{In}_2\text{O}_3$  nanowire · heterostructures · electrical properties · field-emission

One-dimensional (1D) semiconductor heterostructured submicrometer/nanometer-scale materials are of prime interest as building blocks in miniaturized electronic and photonic devices.<sup>1</sup> Recently, significant progress has been made in regard to various axial,<sup>2,3</sup> radial,<sup>4–8</sup> and branched<sup>9–12</sup> 1D heterostructure syntheses. In fact, the successful design and controllable growth of composition-modulated heterostructures may lead to enhanced functionalities, such as emission efficiency and high electron mobility.<sup>13</sup> For example, InAs/InP core/shell nanowire heterostructures have shown a significant increase in electron mobility due to the InP passivation layer.<sup>7</sup> ZnS nanotube–In nanowire-branched heterostructures have exhibited multiply enhanced field-emission properties due to their special geometry. Branched structures attached on a long backbone and having effectively high aspect ratios have demonstrated remarkably large field enhancement.<sup>12</sup> All these exciting works indicate that a design of novel 1D heterostructures

opens up new wide opportunities not only for fundamental science but also for potential utilizations in diverse functional devices.

Monoclinic gallium oxide ( $\beta\text{-Ga}_2\text{O}_3$ ), one of the transparent conducting oxides, is an important wide band gap material. It becomes an n-type semiconductor when synthesized under reducing conditions due to oxygen vacancies.<sup>14</sup>  $\beta\text{-Ga}_2\text{O}_3$  has been considered as a promising material for fabricating optoelectronic devices, spin-tunneling junctions, and gas sensors.<sup>15–18</sup> Although many studies have been devoted to the synthesis and property investigations of various  $\text{Ga}_2\text{O}_3$  nanostructures, such as wire-, ribbon-, cable-, and cactus-like structures,<sup>14,19–23</sup> the analogous reports on 1D  $\text{Ga}_2\text{O}_3$ -based heterostructures have still been lacking. It is believed that the rational synthesis of such heterostructures will allow one to combine different and distinct functionalities of the components and to realize unique properties in such complex systems.

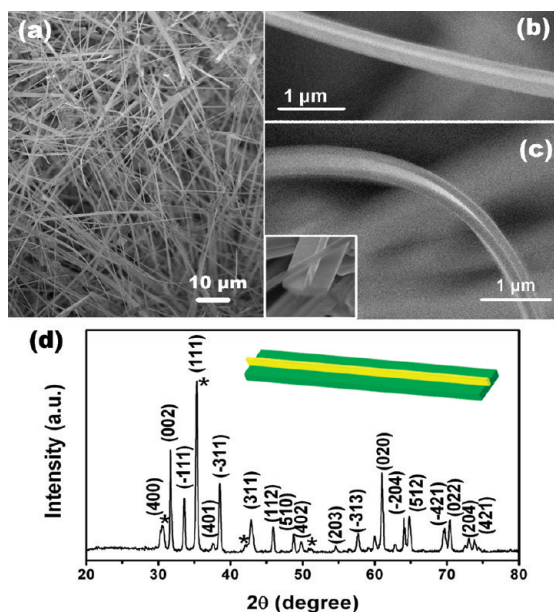
In this paper, we report on the synthesis of 1D  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures where an  $\text{In}_2\text{O}_3$  nanowire is located on the back of a  $\text{Ga}_2\text{O}_3$  nanobelt, thus creating a sort of a “dorsal fin”. The heterostructures have widths of  $\sim 200$ – $500 \text{ nm}$  and lengths of up to tens or hundreds of micrometers. Field-effect transistors (FETs) were designed and fabricated based on individual  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures, and their electrical transport properties were then studied. They exhibited a typical n-type semiconducting behavior and a notable enhancement of conductivity. Moreover, the regarded heterostructures possessed excellent field-emission characteristics: a low turn-on field ( $\sim 1.31$

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**Figure 1.** (a) Low-magnification SEM image of a product. (b, c) High-magnification SEM images of an individual heterostructure revealing the T-shaped cross-section (the inset). (d) XRD pattern of the product.

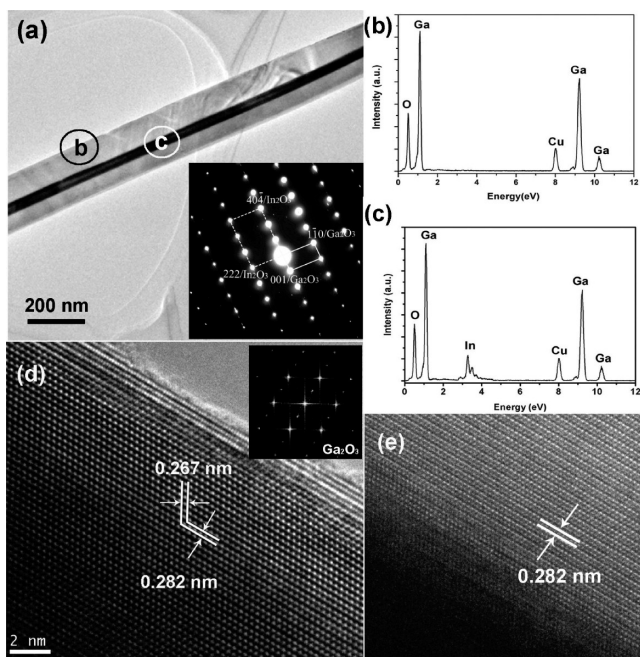
$V/\mu\text{m}$ ) and a high field-enhancement factor (over 4000). Due to their special geometry and enhanced conductivities the field-emission properties of the present nanomaterials not only surpass those of pure  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  components but also rival those of many other prospective 1D nanostructures. The novel structures are envisaged to become highly valuable in field-emitters and electrical and optoelectronic nanodevices.

## RESULTS AND DISCUSSION

After the synthesis, wirelike products were found on the copper foil substrate. The product morphology was checked using scanning electron microscopy (SEM). Figure 1a shows a low-magnification SEM image of the material. It contains numerous whiskers with lengths ranging from several tens to hundreds of micrometers. High-magnification images (Figure 1b,c) reveal that a typical whisker, with a diameter of  $\sim 300$  nm and a length of up to  $\sim 60$   $\mu\text{m}$ , displays a somewhat unusual appearance (see also the Supporting Information, Figure S1). Each heterostructure consists of a nanobelt and the nanowire located on its back forming a sort of a “dorsal fin”; thus, it shows the overall T-shaped cross-section (Figure 1c, inset). Further investigations by transmission electron microscopy (TEM) and X-ray energy dispersive spectroscopy (EDS) suggest that most of the whiskers (more than 80% of the product) are indeed such  $\text{Ga}_2\text{O}_3/\text{In}_2\text{O}_3$  heterostructures, where the nanobelts and nanowires are made of  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$ , respectively (shown later). An X-ray diffraction (XRD) pattern of a product is shown in Figure 1d. Most of the strong peaks can be indexed to a monoclinic structure of  $\text{Ga}_2\text{O}_3$  (JCPDS 76-573). Besides those peaks, some

small peaks marked with star symbols are attributed to a cubic  $\text{In}_2\text{O}_3$  phase (JCPDS 6-416).

The product morphology and microstructures were thoroughly studied using TEM, EDS, and selected area electron diffraction (SAED). Figure 2a is a typical TEM image of an individual heterostructure with a uniform width of 250 nm. The heterostructure appears to exhibit an inner “core” with a diameter of  $\sim 50$  nm. In fact, the inner “core” of a dark contrast in TEM images actually represents the protuberant “dorsal fin” region along the axial direction. EDS spectra collected from the center and edge of the heterostructures (Figure 2b,c) show that the centers are composed of Ga, In, and O, whereas the edge only contains Ga and O. The SAED pattern of the heterostructure (Figure 2a, inset) can be indexed to the  $[110]$  zone axis of  $\beta\text{-Ga}_2\text{O}_3$  and  $[\bar{1}21]$  zone axis of  $\text{In}_2\text{O}_3$ . Thus, the crystallographic relationship is that the  $[110]$  zone axis of a  $\text{Ga}_2\text{O}_3$  belt is parallel to the  $[\bar{1}21]$  zone axis of an  $\text{In}_2\text{O}_3$  wire. Figure 2d is a high-resolution TEM image taken from the edge of the  $\text{Ga}_2\text{O}_3$  nanobelt. It clearly shows a single-crystalline characteristic. The  $d$  spacings of 0.267 and 0.282 nm correspond well to the  $(-111)$  and  $(002)$  plane separations in  $\text{Ga}_2\text{O}_3$ , respectively. The upper-right inset displays the corresponding 2D-Fourier transform (FFT) pattern. All reflections can be assigned to the  $[110]$  zone axis of a  $\beta\text{-Ga}_2\text{O}_3$ . An HRTEM image taken from the interface region of the  $\text{Ga}_2\text{O}_3$  nanobelt/ $\text{In}_2\text{O}_3$  nanowire is shown in



**Figure 2.** (a) Typical TEM image of a heterostructure; (inset) the corresponding SAED pattern, revealing the crystallographic relationship between a  $\text{Ga}_2\text{O}_3$  nanobelt and the  $\text{In}_2\text{O}_3$  nanowire. (b,c) EDS spectra taken from the labeled regions, showing that the center is composed of Ga, In, and O, whereas the edge only contains Ga and O. (d) HRTEM image recorded from the edge of the nanobelt implying its single-crystalline character; (inset) an FFT pattern corresponding to the HRTEM image in panel (d). (e) HRTEM image taken from the nanobelt/nanowire interface region.

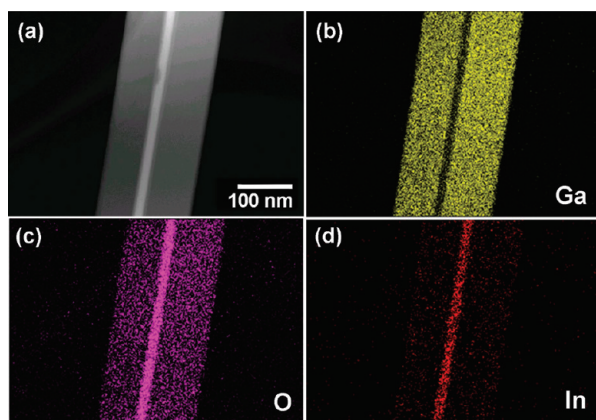


Figure 3. (a) HAADF STEM image of a heterostructure. (b–d) The spatially resolved Ga, In, and O elemental maps.

Figure 2e. The nontransparent dark region can be attributed to an impermeability of the 300 kV electron beam, indicating that a thickness of the protuberant heterostructure region is more than 100 nm.

A detailed chemical analysis was carried out using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and EDS elemental mappings. Figure 3a presents a HAADF STEM image of a heterostructure. The clear bright contrast regions naturally reflect the spatial distribution of In species (In has a larger atomic number than Ga). The elemental maps displayed in Figure 3b–d shed light on the distribution of the constituting elements, which are Ga, In, and O. The strong In L-edge signal originates from the  $\text{In}_2\text{O}_3$  wire. The results clearly demonstrate a well-defined compositional profile of the  $\text{Ga}_2\text{O}_3/\text{In}_2\text{O}_3$  heterostructure.

The formation of an  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructure proceeds via a one-step vapor–solid (VS) growth process. The whole growth process can be proposed as shown in Figure 4. At a high temperature, the reaction between  $\text{Ga}_2\text{O}_3$  and activated carbon takes place as follows:  $\text{Ga}_2\text{O}_3$  (solid) + 2C (solid)  $\rightarrow$   $\text{Ga}_2\text{O}$  (vapor) + 2CO (vapor) and  $2\text{Ga}_2\text{O}$  (vapor) + 4CO (vapor)  $\rightarrow$  4Ga (vapor) + C (solid) + 3CO<sub>2</sub> (vapor).<sup>24</sup> The newly generated Ga or  $\text{Ga}_2\text{O}$  vapors mix with the In vapor (coming from the starting material) and reach the substrate surface. Through the reaction with residual oxygen in the reaction system,  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  clusters are simultaneously formed and act as the nuclei for  $\text{Ga}_2\text{O}_3$  and

$\text{In}_2\text{O}_3$  nanowires. Then the heteroepitaxial growth of 1D  $\text{Ga}_2\text{O}_3/\text{In}_2\text{O}_3$  nanowires occurs due to the lattice match between the two crystals at specific orientations. As aforementioned, the [111] zone axis of the  $\text{Ga}_2\text{O}_3$  nanowire is parallel to the  $[\bar{1}\bar{2}1]$  zone axis of the  $\text{In}_2\text{O}_3$  nanowire. At the same time, the excessive  $\text{Ga}_2\text{O}_3$  clusters may deposit on the side surface of the formed  $\text{Ga}_2\text{O}_3$  nuclei to ensure low energy growth.<sup>25</sup> With an increase in reaction time, the present  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures are formed. Typical SEM images of products obtained after different reaction times (Figure S2, Supporting Information) clearly indicate that the heteroepitaxial growth of 1D heterostructures takes place at very early stages and then finally yields a product with a high aspect ratio.

Field-effect transistors (FETs) based on individual  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures were fabricated, and their electrical properties were studied. The parallel Ti/Au electrodes,  $\sim 3$   $\mu\text{m}$  apart, were fabricated on a single heterostructure, as shown in Figure 5a. Figure 5b presents the gate-dependent drain-source current ( $I_{\text{ds}}$ ) versus voltage ( $V_{\text{ds}}$ ) curves recorded on a representative single FET device. The FET device exhibits notable gate dependence and is conductive, reaching a current of 3.4  $\mu\text{A}$  with a  $V_{\text{ds}}$  of 10 V and a gate voltage ( $V_{\text{g}}$ ) of 40 V. The nonlinear curves indicate that Schottky barriers form between the Ti/Au electrodes and the heterostructure. With a positively increasing  $V_{\text{g}}$  ( $-40$  V  $\rightarrow$  40 V), the conductance of the heterostructure increases, revealing an n-type conductivity. It has been reported that the pure  $\text{Ga}_2\text{O}_3$  nanowires are normally n-type semiconductors due to oxygen vacancies.<sup>14</sup> In this work, the  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures exhibit similar n-type semiconducting behavior. In addition, we also studied the electrical properties of the fabricated devices at different temperatures, in vacuum. Figure 5c displays  $I_{\text{ds}}-V_{\text{ds}}$  curves measured from 300 to 10 K with  $V_{\text{g}} = 0$  V. It can be seen that the conductance of a device decreases as the temperature decreases.

We further estimate the carrier concentration and mobility in the heterostructures. The conventional method to obtain such parameters is to analyze its field-effect behavior using a FET setup. However, herein the Schottky barriers play an important role in the electron transport and the FET model may

result in an underestimate of the mobility.<sup>26</sup> In fact, the present device, as a metal–semiconductor–metal (MSM) structure, can be modeled by two Schottky barriers connected back to back, in series, with a resistor in between. Considering the tunneling current to become

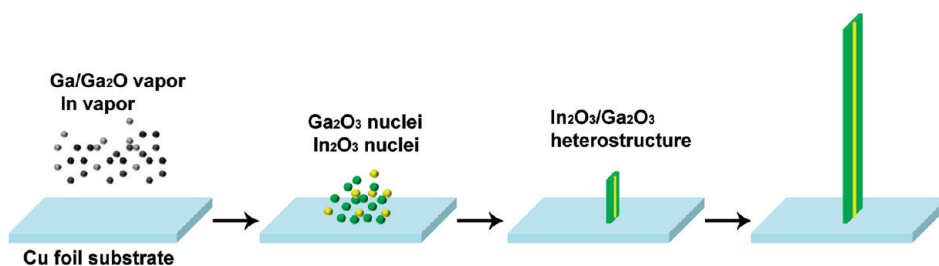


Figure 4. Schematic diagram of the growth of  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures.

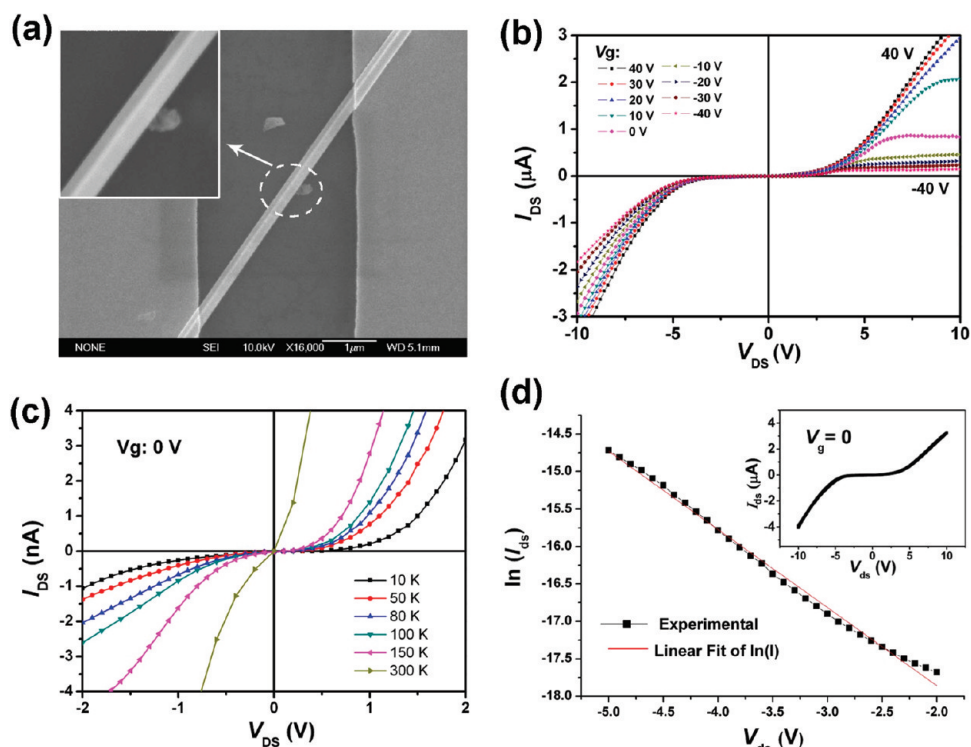


Figure 5. (a) SEM image of an  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructure-based FET; (inset) high-magnification SEM image showing the morphology of the heterostructure. (b)  $I_{\text{ds}}-V_{\text{ds}}$  plots at different  $V_{\text{g}}$ . (c)  $I_{\text{ds}}-V_{\text{ds}}$  curves measured from 300 to 10 K with  $V_{\text{g}} = 0$  V. (d) Experimental and fitted  $\ln(I)$  vs  $V$  plots at an intermediate bias using the  $I_{\text{ds}}-V_{\text{ds}}$  curve at  $V_{\text{g}} = 0$  (inset).

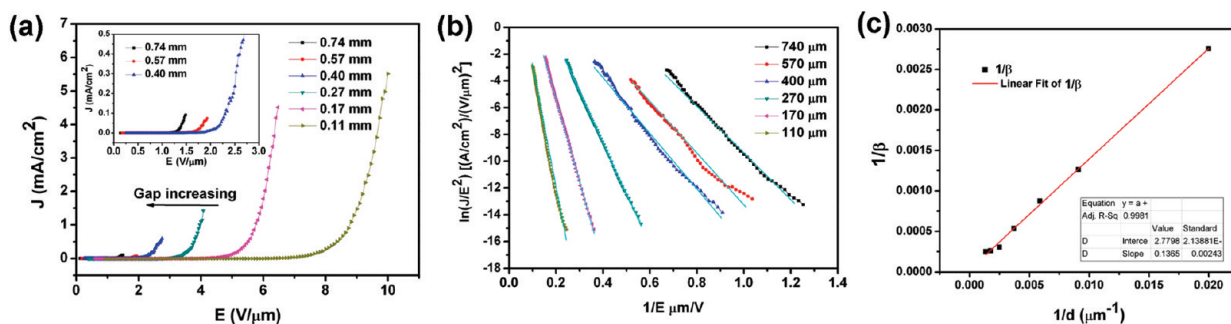
dominant under a reverse bias in a low-dimensional system, thermionic field emission theory is proposed for analyzing the present semiconductor parameters from the two-terminal  $I-V$  curves.<sup>26,27</sup> In detail, the reverse-biased Schottky barrier dominates the total current  $I$  in the intermediate bias regime of the  $I_{\text{ds}}-V_{\text{ds}}$  curve ( $V_{\text{g}} = 0$ )

$$\ln I = \ln(SJ) = \ln S + V \left( \frac{q}{kT} - \frac{1}{E_0} \right) + \ln J_s$$

where  $J$  is the current density through the Schottky barrier,  $S$  is the contact area,  $J_s$  is a slowly varying function of an applied bias, and  $E_0 = E_{00} \coth(qE_{00}/kT)$  with  $E_{00} = \hbar/2[n/(m_n^* \varepsilon_S \varepsilon_0)]^{1/2}$ ,  $n$  is electron concentration,  $m_n^*$  and  $\varepsilon_S$  are the effective mass of an electron and relative permittivity of the material, respectively, and  $\varepsilon_0$  is the permittivity of free space.

The logarithmic plot of a current  $I$  as a function of a bias  $V$  gives approximately a straight line with a slope  $q/(kT) - 1/E_0$ , as shown in Figure 5d. Then  $n$  can be obtained via  $E_0$ , and the electron mobility can be calculated using  $\mu = 1/(nq\rho)$ , with  $\rho$  being the resistivity of the heterostructure, which can be estimated to be  $0.5 \Omega \cdot \text{cm}$ . Applying this procedure to the  $I-V$  curves and assuming the relevant physical constants, such as  $m_n^*$  and  $\varepsilon_S$  (for  $\text{Ga}_2\text{O}_3$ ,  $m_n^* \approx 0.342 m_e$ ,  $\varepsilon_S \approx 10$ ; for  $\text{In}_2\text{O}_3$ ,  $m_n^* \approx 0.3 m_e$ ,  $\varepsilon_S \approx 8.9$ ,  $m_e$  being the free electron mass<sup>28–30</sup>), the electron concentration of the heterostructure is estimated to be  $(4.3-5.5) \times 10^{17} \text{ cm}^{-3}$ , and

the electron mobility is calculated to be  $23-29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We also fabricated standard  $\text{Ga}_2\text{O}_3$  nanobelts under the same reaction conditions but without the use of In reactant and studied their electrical properties (Supporting Information, Figure S3). The resistivity, electron concentration, and mobility in the synthesized  $\text{Ga}_2\text{O}_3$  nanobelts was estimated to be  $10.87 \Omega \cdot \text{cm}$ ,  $1.77 \times 10^{17} \text{ cm}^{-3}$ , and  $3.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. It clearly indicates that the  $\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$  heterostructures possess significantly lower resistivity ( $0.5 \Omega \cdot \text{cm}$ ) (higher conductivity) compared with pure  $\text{Ga}_2\text{O}_3$  nanobelts ( $10.87 \Omega \cdot \text{cm}$ ) as well as  $\text{Ga}_2\text{O}_3$  nanowires ( $300-500 \Omega \cdot \text{cm}$ ) in ref 14. In addition, the electron concentration in an  $\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$  heterostructure is much higher than in a pure  $\text{Ga}_2\text{O}_3$  nanobelt. The present carrier mobility in the  $\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$  heterostructures ( $23-29 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) is about 1 order of magnitude higher than in a standard  $\text{Ga}_2\text{O}_3$  nanobelt ( $3.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and is also larger than in normal  $\text{Ga}_2\text{O}_3$  nanowires ( $6.54 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) in ref 31. Therefore, on the basis of the above comparison, it is believed that the electrical behavior of the present heterostructures is greatly modulated by the  $\text{In}_2\text{O}_3$  nanowire decoration. In particular, the  $\text{In}_2\text{O}_3$  nanowires likely participate in the electron transport together with the  $\text{Ga}_2\text{O}_3$  nanobelts. In addition, the trace amounts of In dopants into  $\text{Ga}_2\text{O}_3$  nanobelts as well as the interface effect within the heterostructure may also contribute to the present electrical conductivity. Although the detailed electrical transport mechanism is



**Figure 6.** Field-emission properties of the heterostructures. (a) Field-emission current density versus an applied field ( $J$ – $E$ ) curves and (b) corresponding Fowler–Nordheim (FN) plots with different vacuum gaps. (c) Relationship between the field-enhancement factor,  $\beta$ , and a vacuum gap,  $d$ . The straight line is the linear fit of the experimental data based on the TRFE model.

still needs further clarification, what we can conclude at present is that, in contrast with standard  $\text{Ga}_2\text{O}_3$  nanostructures, the present  $\text{Ga}_2\text{O}_3$ -based heterostructures demonstrate an enhancement of electron mobility and conductivity. It has been reported that nanostructures with lower resistivity have a better field-emission performance, which is due to the better supply of electrons to the emitting surface.<sup>32</sup> Therefore, the electrical study results imply that the heterostructure may be a valuable field emitter.

In order to study the performance of the  $\text{In}_2\text{O}_3$ -decorated  $\text{Ga}_2\text{O}_3$  heterostructures as a field emitter, field-emission properties were measured in a high vacuum of  $\sim 4.0 \times 10^{-6}$  Pa. Figure 6a shows the emission current density as a function of the electrical field ( $J$ – $E$  plot) measured at different spacings ( $d$ ) between the anode and a sample. When the gap is increased from 0.11 to 0.74 mm, the turn-on field ( $E_{\text{to}}$ ), which is defined as the field required to produce a current density of  $10 \mu\text{A}/\text{cm}^2$ , decreases monotonously from 6.45 to  $1.31 \text{ V}/\mu\text{m}$  (Table 1). The current density at  $6.4 \text{ V}/\mu\text{m}$  is as high as  $4.5 \text{ mA}/\text{cm}^2$  at  $d = 0.17 \text{ mm}$ , and no current saturation is observed. It worth noting that the much lower turn-on field and higher current density of field-emission have been obtained for the present heterostructures, compared with either pure  $\text{Ga}_2\text{O}_3$  nanostructures<sup>14,21,23</sup> or  $\text{In}_2\text{O}_3$  nanostructures,<sup>33,34</sup> as summarized in Table 2. The data suggest that the newly prepared material is a highly valuable field-emitter that rivals previously reported ZnO, ZnS, SiC, Si, and AlN nanowires/nanobelts.<sup>35</sup>

The field-emission current–voltage characteristics were further analyzed using the Fowler–Nordheim (FN) theory

$$J = (A\beta^2 E^2 / \phi) \exp(-B\phi^{3/2} / \beta E)$$

or

**TABLE 1.** Turn-on Field ( $E_{\text{to}}$ ) and Field-Enhancement Factor  $\beta$  Obtained at Different Vacuum Gaps ( $d$ )

$d$ (mm)	0.11	0.17	0.27	0.40	0.57	0.74
$E_{\text{to}}$ ( $\text{V}/\mu\text{m}$ )	6.45	4.23	2.89	1.975	1.7	1.31
$\beta$	793	1142	1875	3287	3827	4002

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

where  $A = 1.54 \times 10^{-6} \text{ A eV}^{-2}$ ,  $B = 6.83 \times 10^3 \text{ eV}^{-3/2} \text{ V } \mu\text{m}^{-1}$ ,  $\beta$  is the field-enhancement factor, and  $\phi$  is the work function of an emitting material. Figure 6b shows the FN plots with different vacuum gaps. The plots are approximately linear, indicating that the FN theory well fits the field-emission behavior of the sample. We can calculate  $\beta$  from the slope of the FN plots in Figure 6b. Considering that the work function of  $\text{Ga}_2\text{O}_3$  is 4.8 eV,  $\beta$  increases from 793 to 4002 under an increasing vacuum gap from 0.11 to 0.74 mm (Table 1). The  $\beta$  value is significantly larger than for other reported  $\text{Ga}_2\text{O}_3$  or  $\text{In}_2\text{O}_3$  nanostructures, as also illustrated in Table 2.

$\beta$  is an important parameter in describing field emission. Generally, the  $\beta$  values are related to the emitter geometry, crystal structure, vacuum gaps, and spatial distribution of emitting centers. Structures with a higher aspect ratio would exhibit stronger field emissions from a given nanostructured material.<sup>35,36</sup> The relationship between  $\beta$  and  $d$  is crucial for fabrication field-emission devices. Figure 6c is a relationship of  $1/\beta$  and  $1/d$ . It shows that  $\beta$  obviously depends on  $d$  with a relationship of  $1/\beta \propto 1/d$ . On the basis of the two-region field-emission model, we found that the experimental data are almost fitted to a straight line and can be approximated by  $1/\beta = h/d + 1/\beta_0$ , where  $h$  is a

**TABLE 2.** Comparative Key Field-Emission Performance Parameters of the Present Heterostructures and the Conventional  $\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  Nanostructures Reported in the Literature<sup>a</sup>

material	turn-on field ( $\text{V}/\mu\text{m}$ )	$\beta$	ref
quasi-aligned $\text{Ga}_2\text{O}_3$ nanowires	6.2	880	14
$\text{Ga}_2\text{O}_3$ –C nanocables	7.73		21
cactus-like $\text{Ga}_2\text{O}_3$ nanostructures	12.6	38.2	23
$\text{In}_2\text{O}_3$ nanowires	2.47 at $0.1 \mu\text{A}/\text{cm}^2$	1810	33
$\text{In}_2\text{O}_3$ nanowires	7 and $10.7$ at $1 \mu\text{A}/\text{cm}^2$		34
$\text{In}_2\text{O}_3/\text{Ga}_2\text{O}_3$ heterostructures	1.31–6.45	793–4002	this work

<sup>a</sup>Here, the turn-on field is defined as the field required to produce a current density of  $10 \mu\text{A}/\text{cm}^2$ . If the other values are used, then this is mentioned separately.

width of the field-emission region near the whisker surface and  $\beta_0$  is the absolute amplification factor, which is intrinsically determined by the emitting surface and independent of  $h$ , and  $d$  is an applied voltage. By fitting the slope and intercept value, the  $h$  and  $\beta_0$  can be determined as  $\sim 136$  nm and  $\sim 4 \times 10^4$ , respectively. The value of  $\beta_0$  is remarkably larger than that of a CNT on an Fe tip ( $\beta_0 = 2.5 \times 10^4$ ) or a CNT film growing on a Si wafer ( $\beta_0 = 7900$ ),<sup>37</sup> ZnO nanorods grown on a Si substrate ( $\beta_0 = 3738$ ),<sup>38</sup> and aligned CdS nanocone arrays ( $\beta_0 = 4933$ ),<sup>36</sup> indicating excellent field enhancement in the present In<sub>2</sub>O<sub>3</sub>-decorated Ga<sub>2</sub>O<sub>3</sub> structures.

The high field-enhancement and low turn-on field values indicate that the present In<sub>2</sub>O<sub>3</sub>-decorated Ga<sub>2</sub>O<sub>3</sub> heterostructures, despite their submicrometer dimensions, possess excellent field-emission characteristics. As we discussed above, the improved electrical properties (increased conductivity and mobility) are important for the observed field emission behavior. We can conclude that a high aspect ratio, good crystallinity, special geometry, and enhanced conductivity are responsible for these field-emission characteristics. It is believed that the growth of the analogous heterostruc-

tures with reduced dimensions will be an effective route to further enhance their field-emission performance and obtain more efficient emitters.

## CONCLUSIONS

Novel 1D In<sub>2</sub>O<sub>3</sub>-decorated Ga<sub>2</sub>O<sub>3</sub> heterostructure whiskers were synthesized via a simple catalyst-free vapor-solid method. The heterostructure consists of a primary Ga<sub>2</sub>O<sub>3</sub> nanobelt and the In<sub>2</sub>O<sub>3</sub> nanowire (in a shape of a "dorsal fin") and as a whole displays the T-shaped cross-section. Field-effect transistors were fabricated based on individual In<sub>2</sub>O<sub>3</sub>/Ga<sub>2</sub>O<sub>3</sub> heterostructures. These showed n-type characteristics. The heterostructures possess lower resistivity and higher electron mobility compared with pure Ga<sub>2</sub>O<sub>3</sub> nanostructures. Field-emission measurements showed the remarkably low turn-on field of ca. 1.31 V/ $\mu$ m at a current density of 10  $\mu$ A/cm<sup>2</sup> and a vacuum gap of 0.74 mm. The field-enhancement factor  $\beta$  was calculated to be over 4000. The excellent field-emission characteristics are attributed to a high aspect ratio, good crystallinity, special geometry, and high conductivity of the present heterostructures. This new material may have a high promise for novel field-emitting, electronic and optoelectronic nanodevices.

## METHODS

The synthesis of In<sub>2</sub>O<sub>3</sub>/Ga<sub>2</sub>O<sub>3</sub> heterostructures was carried out in a conventional horizontal furnace. A mixture of Ga<sub>2</sub>O<sub>3</sub> (500 mg), In (100 mg), and activated carbon (50 mg) was put in a quartz boat. A copper foil (10 mm  $\times$  20 mm) was first cleaned using alcohol in an ultrasonic cleaner and then capped on the quartz boat horizontally. After the boat was transferred into a quartz tube mounted in the furnace, the system was purged with 200 sccm Ar gas for 1 h. Then the furnace was heated to 1000 °C in 30 min and kept at this temperature for 1 h with the Ar flow kept constant. After the system was cooled to room temperature, a brown product was found deposited onto the Cu substrate.

An as-prepared product was characterized by a scanning electron microscope (SEM, JEOL, JSM-6700F), a powder X-ray diffractometer (XRD, RIGAKU, Ultima III, 40 kV/40 mA with Cu K $\alpha$  radiation), a 300 kV high-resolution field-emission transmission electron microscope (TEM, JEOL, JEM-3000F) equipped with an energy-dispersive X-ray analyzer (EDX), and a high-angle annular dark-field scanning transmission electron microscopy detector (HAADF-STEM) (JEOL JEM-3100FEF).

For the fabrication of FET, In<sub>2</sub>O<sub>3</sub>-decorated Ga<sub>2</sub>O<sub>3</sub> heterostructures were first dispersed in alcohol and then deposited onto a thermally oxidized Si substrate covered with a 600 nm SiO<sub>2</sub> layer at a desired density. The Ti/Au (10 nm/100 nm) interdigitated electrodes were patterned on top of the heterostructures using optical lithography with the assistance of a pre-designed mask and electron beam deposition.

The field-emission properties were studied at room temperature in a high vacuum chamber ( $3 \times 10^{-6}$  Pa) using a 1 mm<sup>2</sup> cross-sectional area Al anode. A dc voltage sweeping from 100 to 1100 V was applied to the samples.

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*Supporting Information Available:* Low- and high-magnification SEM images of In<sub>2</sub>O<sub>3</sub>/Ga<sub>2</sub>O<sub>3</sub> heterostructures, SEM images of products obtained after different reaction times, and the electrical property analysis of pure Ga<sub>2</sub>O<sub>3</sub> nanobelts synthesized under similar reaction conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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