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Field emission enhancement from patterned gallium nitride nanowires

D K T Ng[1,2], M H Hong[1,2], L S Tan[1], Y W Zhu[3,4] and C H Sow[3,4]

[1] Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117576, Singapore
[2] Data Storage Institute, DSI Building, 5 Engineering Drive 1, Singapore 117608, Singapore
[3] National University of Singapore, Nanoscience and Nanotechnology Initiative, S13, 2 Science Drive 3, Singapore 117542, Singapore
[4] Department of Physics, National University of Singapore, 2 Science Drive 3, Singapore 117542, Singapore

E-mail: HONG_Minghui@dsi.a-star.edu.sg

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Abstract
Patterned gallium nitride nanowires have been grown on n-Si(100) substrates by pulsed laser ablation. The nanowires are patterned using a physical mask, resulting in regions of nanowire growth of different density. These gallium nitride nanowires are single-crystalline with hexagonal wurzite structures. The electrical transport measurements of individual GaN nanowires show near-linear current–voltage characteristics. The estimated electron densities of these individual GaN nanowires range from 1.8–6.8 × 10^{18} cm^{-3}. The field emission characteristics of these patterned gallium nitride nanowires show a turn-on field of 8.4 V μm^{-1} to achieve a current density of 0.01 mA cm^{-2} and an enhanced field emission current density as high as 0.96 mA cm^{-2} at an applied field of 10.8 V μm^{-1}. The field emission results indicate that, besides crystalline quality as well as the low electron affinity of gallium nitride, density difference in the nanowires growth greatly enhances their field emission properties by reducing the screening between nanowires.

1. Introduction

Field emitters have wide applications in vacuum microelectronics, including ultrahigh speed devices, electron beam lithography, and low power and high brightness field emission (FE) flat panel displays. As a wide-bandgap semiconductor, gallium nitride (GaN) has attracted a lot of attention as a material for FE devices [1]. It has strong chemical and mechanical stability and a low electron affinity of 2.7–3.3 eV [2–4]. There are many research efforts into the investigation of FE from GaN films [5, 6] and pyramid arrays [7]. It was reported that the pyramid or roughing shapes of GaN increase the field enhancement factor (β), lowering the applied voltage for the electron emission. Thus, further enhancement of FE characteristics is anticipated by the one-dimensional (1D) structures of GaN.

Meanwhile, the substrates' FE performance of continuous 1D nanostructure films, though higher than those of bulk films, is dampened by the screening effect between the densely packed nanostructures. Patterning the nanostructures was introduced to solve this problem for further FE enhancement [8]. It has been shown that nanotubes arranged in regularly patterned arrays of bundles, with bundle diameter and array spacing of the order of a few micrometers, give much greater FE current densities than dense mats of nanotubes, thin films of nanotubes or arrayed individual nanotubes [9]. Such arrays appear ideal to be integrated into nanodevices for high-intensity electron beams from FE sources. With the recent rapid development in nanoscience and nanotechnology, patterning of field emitters is one of the highly promising approaches for many multi-dimensional and multi-functional system applications, including patterned electron emitting displays, multi-analyte sensors, multi-channel microreactors and microfluidic devices. In addition, the resistance of the nanowires can also affect the emission current if the resistance is high [10]. A low resistance will give higher FE while a higher resistance can limit the maximum emission current.

Till now, the FE from continuous GaN nanowire films synthesized by chemical vapor deposition (CVD), hydride vapor phase epitaxy (HVPE) and thermal evaporation has been reported [11–16]. Compared to these techniques, pulsed laser ablation (PLA) can create a highly energetic growth precursor, leading to the formation of non-equilibrium growth conditions. High-quality nanowires can be obtained at a fairly low substrate temperature. Furthermore, PLA can be performed in a background gas or in conjunction with a source of reactive species and offers more flexibility than other conventional techniques [17]. In this paper, we present a direct and non-toxic way to grow patterned single-crystalline GaN nanowires on an n-Si(100) substrate using PLA. The electrical transport properties of individual GaN nanowires were studied and their enhanced FE characteristics were investigated. To the best of our knowledge, this is the first time that the FE properties of patterned GaN nanowires synthesized by PLA are reported.

2. Experimental details

The precursor material for growing GaN nanowires was a 1-inch diameter GaN target (99.95% purity). This target was loaded into the deposition chamber and held by a rotating target holder for uniform ablation to avoid drilling through by the continuous irradiation of intense laser pulses. After evacuating the chamber to a base pressure of 5.7×10^{-7} Torr, the chamber was filled with 99.999% purified nitrogen (N_2) at a flow rate of 100 sccm. A chamber pressure of 100 mTorr was maintained during PLA. The laser ablation was conducted with a KrF excimer laser (248 nm, 23 ns (full width at half-maximum), Lambda Physik Germany, COMPEX 102) at a laser fluence of 5.0 J cm^{-2} for 1 h at a pulse repetition rate of 3 Hz. Patterned n-Si substrates (using a transmission electron microscopy (TEM) Cu grid as a physical mask) coated with a 5 nm gold (Au) thin film by an electron-beam evaporator were placed on a substrate holder. It was positioned 3–5 cm perpendicularly opposite to the GaN target. The temperature of the substrates was kept at 700 °C during the synthesis of the nanowires. After the nanowire growth, the substrates were allowed to cool down to 100 °C and below in N_2 ambient to prevent oxidation. The special feature of the PLA process is that each laser pulse ablation generates a large quantity of Ga and N species ($\sim 10^6$ atoms/pulse), which are instantaneously deposited onto the Au catalyst surface. The time interval between two laser pulses was 333 ms for a repetition rate of 3 Hz. This allowed sufficient time for the deposited GaN species to interact with the catalyst. The morphology of the nanowires grown was examined using a field emission scanning electron microscope (FESEM, Hitachi S4100) and their crystal structure was examined with TEM (JEOL JEM-2010F with STEM option). The electrical transport measurements were done on individual GaN nanowires using a dual-beam FIB (FEI Quanta 200—3D FIB—SEM) induced metal deposition technique. The nanowires were dispersed on 300 nm thick silicon dioxide film (SiO_2) grown on n-Si by wet oxidation. Platinum (Pt) square contact pads of 5 μm by 5 μm (150 nm thick) were made 3–5 μm away from the single nanowire connected by thin Pt metal lines to these individual nanowires. The electrical properties of each single nanowire were measured using two 70 nm tungsten probes (Cascade Microtech four-probe system). FE measurements for the as-grown GaN nanowires were conducted in a vacuum chamber at a pressure of 2×10^{-6} Torr and room temperature.

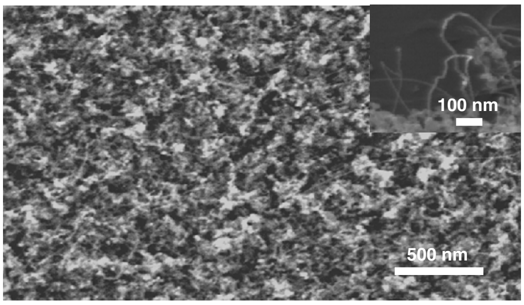

Figure 1. FESEM images of the as-grown GaN nanowires showing a top view and close-up view (inset) of some individual nanowires.

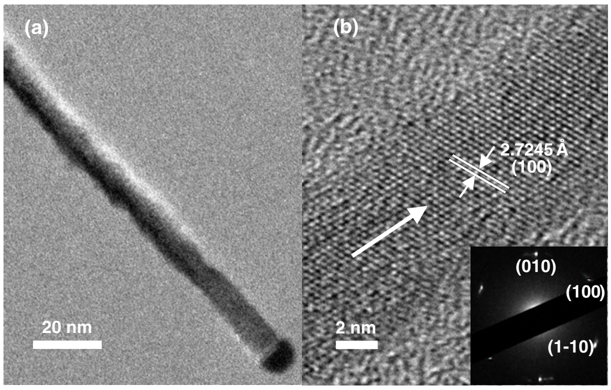

Figure 2. TEM images of (a) low magnification and (b) high resolution single GaN nanowire revealing the lattice spacing of the GaN nanowire. Inset shows the nano-beam electron diffraction of the nanowire.

3. Results and discussion

Figure 1 shows the top-view FESEM image of the GaN nanowires grown on the n-Si substrate. The diameters of these nanowires range from 10 to 40 nm and their lengths range from 1–1.5 μm. The inset shows the close-up view of individual nanowires with the diameters around 10 nm. PLA nanowire growth results in different densities of nanowires growth in different regions. The Au catalyst was patterned by a TEM grid as a physical mask. Figure 2(a) shows the low-magnification TEM image of an as-grown GaN nanowire after ultrasonic dispersion in alcohol solution during TEM sample preparation. The diameter of the nanowire was measured to be around 10 nm. At the tip of the nanowire is a dark spherical-like image, which is the Au/Ga tip functioning as the nucleation site for the catalyzed growth of each nanowire by the vapor–liquid–solid mechanism [18]. Figure 2(b) shows the high-resolution TEM image of the nanowire in the (100) planes with a lattice spacing of 2.72 Å from the clear lattice fringes. These nanowires are generally grown in the ⟨010⟩ orientation. The growth direction is indicated by the white arrow. A nano-beam electron diffraction pattern (inset of figure 2(b)) can be indexed to the [001] zone axis of a hexagonal wurzite GaN crystal. Both the high-resolution TEM image and diffraction pattern indicate the growth of good-quality single-crystalline GaN nanowires.

The electrical transport measurements of these as-grown individual GaN nanowires were measured. Figure 3 shows

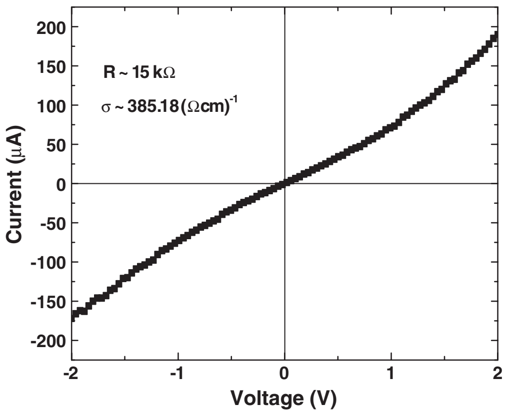

Figure 3. I–V characteristic of an individual GaN nanowire.

the current–voltage (I–V) characteristics of the electrical measurement of a single GaN nanowire. Using the as-deposited Pt contacts, figure 3 shows a near-linear I–V trend. Though the resistance obtained from this I–V trend involved both the resistance of the nanowire and the contacts, this measured resistance can be a rough estimate of the nanowire's characteristics. The measured resistance of this GaN nanowire is around 15 kΩ. A series of electrical measurements were made for four other GaN nanowires and their resistances ranged from 12 to 82 kΩ. The length and diameter of each of these five nanowires were measured and the calculated conductivities of the nanowires ranged from 43.95 to 703.64 $(\Omega\ \mathrm{cm})^{-1}$. Since GaN is intrinsically n-type, its conductivity can be related to its carrier density through the expression [19]

$$\sigma = en\mu, \tag{1}$$

where e is the elemental charge, n is the electron density and μ is the electron mobility. Although direct extraction of carrier densities in these GaN nanowires cannot be made without more significant carrier modulation, carrier densities may be estimated using GaN nanowire electron mobilities from the literature [20]. Substituting the calculated conductivities and the mobility range given [20] (150–650 $\mathrm{cm^2\ V\ s}$) into equation (1), the estimated electron densities of these individual GaN nanowires ranged from 1.8 to $6.8 \times 10^{18}\ \mathrm{cm^{-3}}$. These high electron densities (due to low nanowire resistivity) compared to bulk GaN can support high field emission without any saturation and help in mitigating self-heating under high current.

The I–V characteristics of FE from these patterned single-crystalline GaN nanowires were investigated. The FE measurement system consisted of a vacuum chamber at a low pressure of 2×10^{-6} Torr, using a two-parallel-plate configuration at a vacuum spacing of 100 μm, as described in [21]. A conducting indium tin oxide (ITO) glass was used as the anode. The FE current density as a function of the macroscopic electric field of the GaN nanowires is shown in figure 4(a). The turn-on field of 8.4 V $\mu\mathrm{m}^{-1}$ was obtained based on the definition for the field to produce an emission current density of 0.01 mA cm^{-2}. The emission current density reached 0.96 mA cm^{-2} at an applied field of 10.8 V $\mu\mathrm{m}^{-1}$. This result is a tremendous improvement

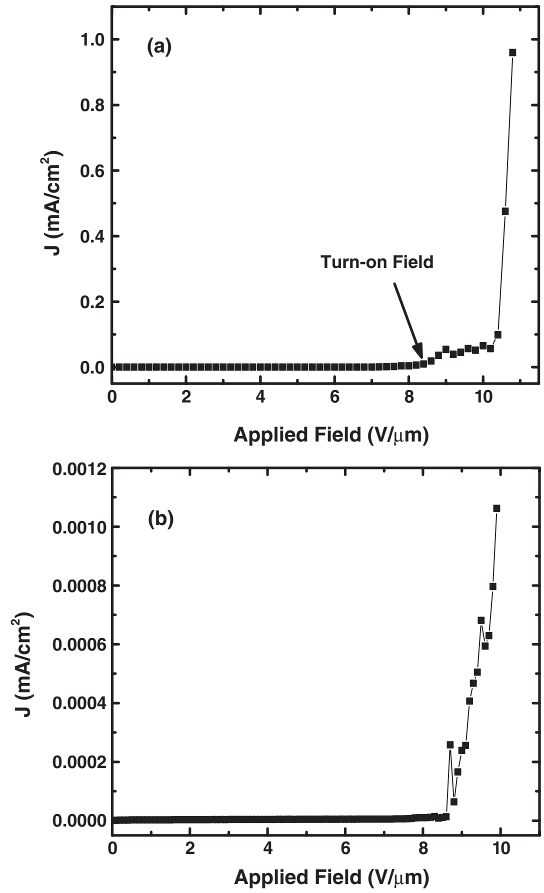

Figure 4. FE current density of the (a) patterned GaN nanowires and (b) continuous GaN nanowire films as a function of the applied electric field.

from that of continuous GaN nanowire films grown by PLA without patterning under the same experimental conditions. For continuous GaN nanowire films, the FE current densities obtained were unstable (figure 4(b)). They increased to a maximum of 0.001 mA cm^{-2} at an applied field of 10 V $\mu\mathrm{m}^{-1}$ and were then burnt. Compared to the FE current density of 0.064 mA cm^{-2} at 10 V $\mu\mathrm{m}^{-1}$ obtained from the patterned GaN nanowires, the FE current density from continuous GaN films at 10 V $\mu\mathrm{m}^{-1}$ is 64 times lower. Continuous films suffer from the screening effect due to electrostatic screening between adjacent emitters. Though the field amplification of an emitter is determined by the radius of curvature at the tip as well as the height of the wire over the substrate, the distance between neighboring emitters has a decisive influence due to the screening effects. The electric field near the apex of emitters decreases with decreasing spacing between them. Hence, patterned nanowires prove to have a higher and more stable emission current than continuous nanowire films.

On the basis of an ideal metal–vacuum interface, a simple Fowler–Nordheim (FN) model (figure 5(a)) describes the relationship between the emission current density and the electric field applied on the metal surface. As FE involves the extraction of electrons from a solid by tunneling through the surface potential barrier, the emitted current depends directly on the local electric field at the emitting surface and

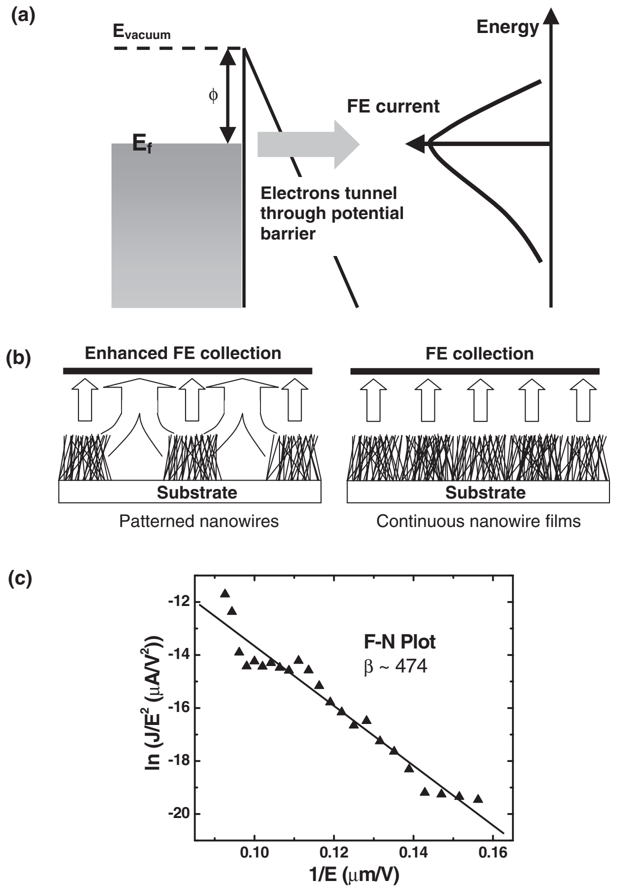

Figure 5. (a) FN model for a metallic emitter. (b) Schematic diagram of FE magnitude of patterned GaN nanowires compared to continuous GaN nanowire films. (c) FN plot of patterned GaN nanowires.

its work function. The emitted current is highest as the electrons overcome the potential barrier and move from the Fermi level (E_f) to the vacuum state. Figure 5(b) shows a schematic diagram of the FE magnitude for patterned GaN nanowires compared to continuous GaN nanowire films. The FE magnitude is greater at regions where the nanowires are near the edges of the Au catalyst pattern due to reduced screening effect. Therefore, the total current collected during FE measurement for patterned nanowires is much greater compared to that of continuous nanowire films.

Comparing the FE properties of these patterned GaN nanowires with those of GaN nanowires using other growth methods [11–16], the turn-on field of 8.4 V μm^{-1} at a current density of 0.01 mA cm^{-2} is reasonably low for good FE properties of GaN nanowires. The peak current density of 0.96 mA cm^{-2} at an applied field of 10.8 V μm^{-1} is also high enough for FE device applications. Such good FE properties from these patterned GaN nanowires grown by PLA further enhance their potential as good candidates for the field emitters.

The FN plot of the patterned GaN nanowires is shown in figure 5(c). A straight line fit of the FN scattered plot reveals the electron emission due to FN tunneling. From the slope of the straight line, the field enhancement factor (β) can be calculated using the FN equation expressed as [22]

$$J = A\left(\frac{\beta^2 V^2}{\phi d^2}\right)\exp\left(-\frac{B\phi^{3/2}d}{\beta V}\right), \qquad (2)$$

where J is the current density (μA μm^{-2}), $A = 1.4$ and $B = 6440$ are constants, ϕ is the work function (eV), d is the distance (μm) between the anode and the cathode and V is the applied voltage (V). Assuming that the work function of GaN is 4.1 eV, the field enhancement factor β is estimated to be 474. This β value reflects the degree of the FE enhancement of the tip shape on a planar surface. It is dependent on the geometry of the nanowires, the crystal structure and the density of emitting points. Compared to the β values of GaN nanowires already reported [13, 15], the β value of 474 reported here is lower. This lower value may be attributed to the shorter length of GaN nanowires in this study as those with higher β reported have lengths ranging from several micrometers to tens of micrometers. Since the GaN nanowires in this study have lengths ranging from 1 to 1.5 μm, the lower β value calculated is considered reasonable.

4. Conclusion

In summary, patterned GaN nanowires were synthesized on n-Si substrates by PLA using the vapor–liquid–solid mechanism with Au as the catalyst. TEM grids were used as physical masks to create the patterns. The nanowires were single-crystalline with hexagonal wurtzite structures, grown along the ⟨010⟩ direction. The nanowire diameters ranged from 10 to 40 nm with lengths ranging from 1.0 to 1.5 μm. Electrical transport measurements on individual GaN nanowires showed a near-linear I–V trend. The resistances calculated ranged from 12 to 82 kΩ. In addition, the electron densities were estimated to be in the range of 1.8–6.8 × 10^{18} cm^{-3}. This high electron density (due to low nanowire resistivity) compared to bulk GaN can support high field emission without any saturation. FE measurements revealed better FE properties on these patterned GaN nanowires compared to continuous GaN nanowire films grown by PLA. These patterned GaN nanowires had a turn-on field of 8.4 V μm^{-1} at a current density of 0.01 mA cm^{-2} and a high FE current density of 0.96 mA cm^{-2} at an applied field of 10.8 V μm^{-1}. These results indicate that density difference in the nanowires growth further enhances their FE properties, in addition to good crystalline quality, low resistivity as well as the low electron affinity of GaN nanomaterials.

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