Synthesis and Field Emission Characteristics of Ga_2O_3 Nanorods with Ultra-Sharp Tips

Yavuz Bayam[1,2], Logeeswaran VJ[1], Aaron M. Katzenmeyer[1], Rebecca J. Chacon[1], Michael C. Wong[1],
Charles E. Hunt[1], and M. Saif Islam[1]

***Abstract-* We successfully synthesized β-Ga_2O_3 nanorods with ultra-sharp tips without use of a catalyst. The nanorods were produced by heating a GaAs wafer in a CVD chamber. The morphology and structure of the nanorods were characterized by scanning electron microscopy(SEM), Energy Dispersive X-ray Spectroscopy (EDS) and Raman-Scattering Spectroscopy. The field emission characteristics demonstrated a turn-on field of about 2.1 $V\mu m^{-1}$ and the threshold electric field of 5.6 $V\mu m^{-1}$.**

I. INTRODUCTION

Recently, numerous vertically-oriented one-dimensional nanostructures fabrication methods, using bottom-up synthesis processes have attracted interest owing to their simplicity of synthesis and high electromechanical performance. Materials such as carbon nanotubes (CNTs), wide band-gap semiconductors, metal nanowires and several oxides such as In_2O_3, ZnO, SnO_2 and Ga_2O_3 have stimulated considerable interest. Some of these materials have low electron affinity and/or high chemical stability. Monoclinic gallium oxide (β-Ga_2O_3) is an important metal oxide semiconductor with a wide band gap (E_g = 4.9 eV). The conduction [1] and luminescence [2] properties makes it a good candidate for optoelectronic applications such as flat panel displays, solar energy devices, and high temperature stable gas sensors [3].

Field emission, a very well understood quantum effect, is a good source for high-brightness electrons with low energy spread. Under high electric field, electrons near the Fermi level escape to the vacuum level by overcoming the energy barrier. For many applications using field emission, the materials should exhibit very low threshold emission fields and a high degree of stability at high current density. A low work-function and a large field enhancement factor contribute to a low threshold field of electron emission. While work-function is an intrinsic material property, the field enhancement factor (FEF) predominantly depends on the geometry of the emitters. Tedious and costly top-down processing techniques have been demonstrated to fabricate field emission tips with diminishingly small radius [4, 5], although most such emitters have finite lifetime and exhibit performance degradation over a short period.

Zhan et. al, reported the first field emission properties of Ga_2O_3-C nanocables with a turn on field of 7.73 $V\mu m^{-1}$ [6] and Cao et al. recently reported cactus-like gallium oxide nanostructures with a threshold electric field of 12.6 $V\mu m^{-1}$.[7].

In this paper, we report on the catalyst-free synthesis and characterization of β-Ga_2O_3 nanorods with ultra-sharp tips by heating a GaAs wafer in a tube furnace. The structures exhibited excellent field emission characteristics with a turn-on field of ~2.1 $V\mu m^{-1}$ and the threshold electric field of 5.6 $V\mu m^{-1}$.

II. SAMPLE PREPARATION

The Ga_2O_3 nanorods with ultra-sharp tips were grown in a horizontal alumina tube inserted in a furnace as shown in Fig. 1. The tube was continuously pumped down to 749 x 10^{-3} Torr. The carrier gas that was used was Argon at a flow rate of 100sccm flow, while the residual O_2 in the alumina tube acted as the reaction gas. The Zn-doped GaAs(100) substrate was first ultrasonically cleaned and then placed in an alumina boat and the boat was placed at a distance of ~12cm from the center of alumina tube facing downstream to the flow of carrier gas. The temperature distribution along the tube is not uniform during the heating process. The maximum temperature is the highest at the center of the tube and is ~800°C where the substrates are located. Prior to heating the tube, Argon was introduced into the system to flush out the tube for ~20 min. Then the furnace temperature was ramped up to 1050°C and held constant for ~40 min. After this process, the furnace was cooled down to room temperature. Upon retrieving the sample, a layer of white wool like film was observable on the surface of GaAs substrate.

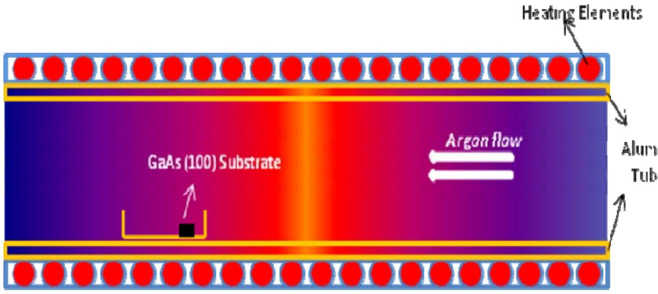

Fig.1. Schematic illustration of experimental setup

III. RESULTS & DISCUSSION

The resulting films were characterized using Scanning Electron Microscopy (SEM), Raman Spectroscopy and Energy Dispersive X-ray Spectroscopy (EDS).

---

[1] Department of Electrical and Computer Engineering, University of California at Davis, Davis CA 95616 USA, Email: saif@ece.ucdavis.edu.
[2] Department of Computer Engineering, Sakarya University, 54187 Sakarya, Turkey.

978-1-4244-2104-6/08/$25.00 ©2008 IEEE.

A. Raman Spectroscopy

The Raman Spectra of Ga_2O_3 nanorods were acquired by a Renishaw RM1000 Research Laser Raman Microscope. Fig.2 shows the room temperature Raman scattering spectra of Ga_2O_3 nanorods under the excitation wavelength of 514nm. Raman peaks were obtained at 191, 310, 337, 406, 466, 621, 646 cm^{-1}. These peaks are an exact match with single crystal β-Ga_2O_3 [8, 9].

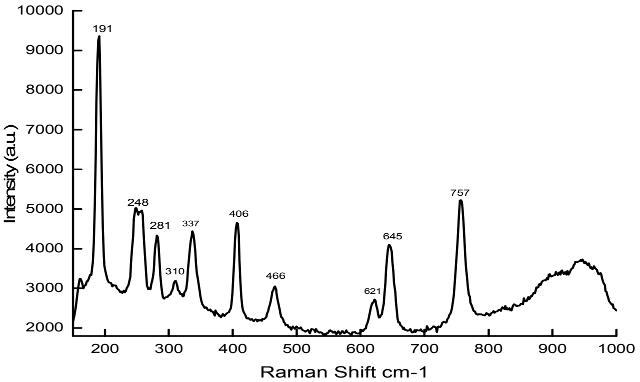

Fig.2 The Raman Spectra of Ga2O3 nanorods. The peaks are obtained at 191, 310, 337, 406, 466, 621, 646 cm-1. These peaks are an exact match with single crystal β-Ga2O3.

B. Scanning Electron Microscopy

For surface morphology characterization, the FEI XL30-SFEG Scanning Electron Microscope was employed. The SEM images revealed that Ga_2O_3 nanorods intensely grew on the substrate and most of them have ultra-sharp tips on the top facet with a large aspect ratio. The diameter of the nanorods varies from 200nm up to 1µm. Figures 3(a)-3(b) show the overall nanorod images while 3(c)-3(d) show the magnified SEM images of Ga_2O_3 nanorods and ultra-sharp tips.

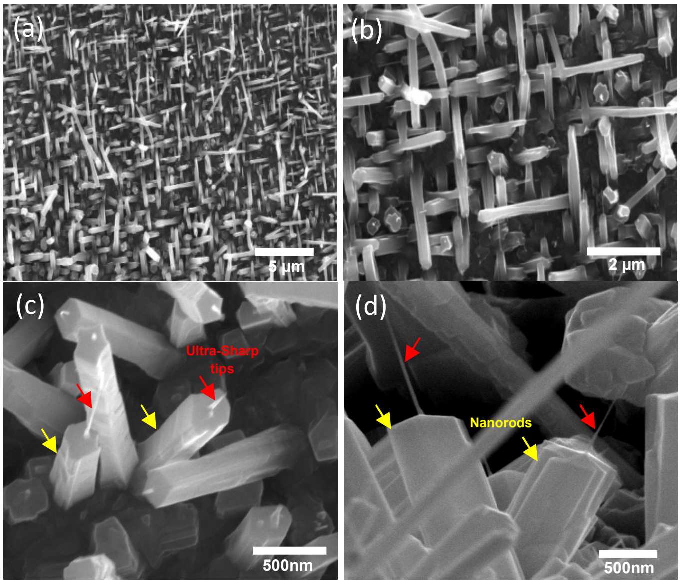

Fig.3 (a-b) low magnification (c-d) high magnification SEM images of Ga_2O_3 Nanorods (yellow arrows) and Ultra-Sharp tips (red arrows)

C. Selected Area Energy Dispersive X-ray Spectroscopy (EDS)

The chemical composition of Ga_2O_3 nanorods were studied by Energy Dispersive X-ray Spectroscopy (EDS) module attached to the SEM as shown in Figure 4. The EDS data show that the main composition of the nanorods reveals the presence of Ga and O_2 while the As signal is from the substrate.

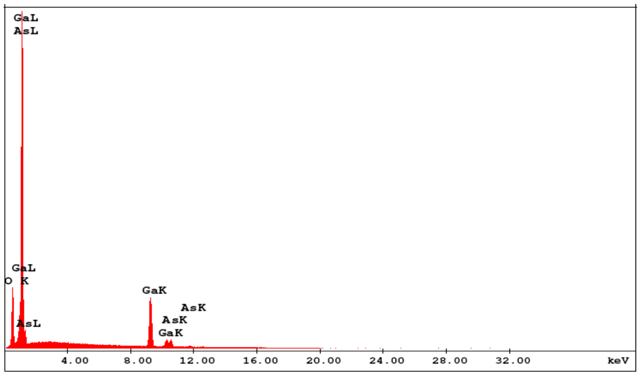

Fig.4. EDS measurement of Ga_2O_3 nanorods show that the main composition of the nanorods is Ga and O_2 whereas the As signal is traceable to the substrate.

D. Field Emission Characterization

The schematic for the field emission experiments are shown in Figure 5. We performed the measurements in a high-vacuum chamber (~$15x10^{-6}$ Pa). The sample was fixed onto an Aluminum SEM sample holder that also functioned as the cathode while the stainless steal plate was used as an anode. The distance between the anode and the ultra-sharp tips of the Ga_2O_3 nanorods was ~1mm. The measured emission area was ~$76.5mm^2$. The field emission I–V curves were analyzed using the Fowler–Nordheim (FN) equation for the field emission:

$$J = (A\beta^2E^2/\Phi)exp[-B\ \Phi^{3/2}(\beta E)^{-1}] \qquad (1)$$

Where J is current density, E is applied electric field at the tip, A, B are constants, and Φ is the work function which is estimated to be 4.15eV for Ga_2O_3.[10] Figure 6 shows the emission current density vs applied electric field (J-E) from the Ga_2O_3 nanotips. The inset shows the F-N plots. F-N plots showed linear characteristic which indicates field emission from Ga_2O_3 nano structures.

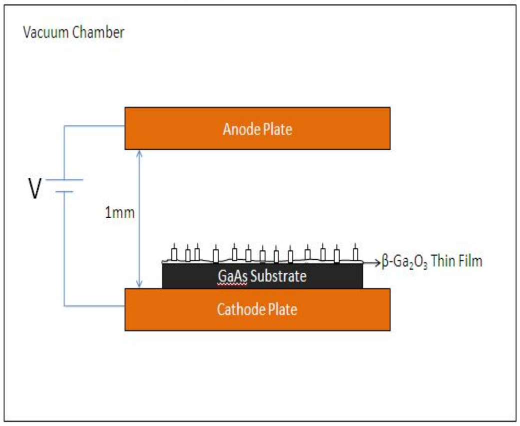

Fig.5. Schematic of the Field Emission measurement system

The turn-on field which represents the electric field required to generate an emission current density of 10 μAcm^{-2} was about 2.1Vμm^{-1}. The threshold field which represents the electric field required to generate an emission current density of 10 mAcm^{-2} was about 5.6Vμm^{-1}. It is important to note that the turn-on voltage of ~2.3Vμm^{-1} is as low as nanostructured diamond 3-5 Vμm^{-1})[11] and highly oriented single wall carbon nanotubes (0.7-3.9 Vμm^{-1})[12]. These excellent field emission characteristics make Ga_2O_3 nanorods a great candidate for industrial field emission applications.

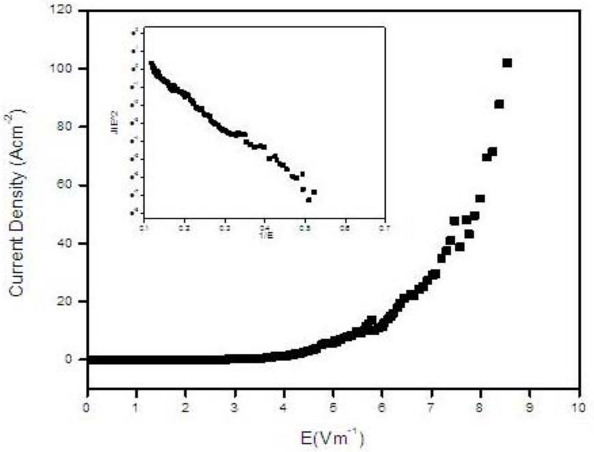

Fig.6.The emission current density from the Ga_2O_3 nanotips vs applied field (*J-E*). The inset is the F-N plots.

Table 1 details the comparison between the published data on the turn-on field and the threshold field with our Ga_2O_3 ultra-sharp tip nanorods.

TABLE 1. A comparison of the field emission parameters of various 1D structures

1D nanostructures	**Turn-on field (Vμm^{-1})**	**Threshold Field (Vμm^{-1})**
Ga_2O_3 Nanowires With Ultra-Sharp Tip	***2.1***	***5.6***
Carbon nanotubes[13]	0.75	1.6
CN_X Nanotubes[14]	2-3	5.5 at 3mA/cm^2
BCN_X Nanotubes[14]	2-3	5.5 at 3mA/cm^2
AlN Nanotips[15]	4.7	10.6
GaAs Nanowires[16]	2	6.5
GaN Nanobelts[17]	1.3	2.3
NiO Nanorods[18]	11.5	6.5
ZnO Agavelike NWs[19]	2.4	4.3
Cactus-like Ga_2O_3 Nanostructures[20]	12.6	23.2
Ga_2O_3-C Nanocables[6]	7.73	8.45

IV. CONCLUSION

We have demonstrated a catalyst-free synthesis and characterization of β-Ga_2O_3 nanorods with ultra-sharp tips by heating a GaAs wafer in a tube furnace. The structures exhibited excellent field emission characteristics with a turn-on field of ~2.1 Vμm^{-1} and the threshold electric field of 5.6 Vμm^{-1}.

REFERENCES

1. H. Zoltan, et al., “Role of oxygen vacancy defect states in the n-type conduction of beta-Ga_2O_3,” *Journal of Applied Physics*, vol. 86, no. 7, 1999, pp. 3792-3796.
2. Y.W. Wang, et al., “Preparation and characterization of ordered semiconductor CdO nanowire arrays,” *Journal of Materials Science Letters*, vol. 20, no. 18, 2001, pp. 1687-1689.
3. Z. Liu, et al., “O_2 and CO sensing of Ga_2O_3 multiple nanowire gas sensors,” *Sensors and Actuators B* vol. 129, 2008, pp. 666-670.
4. I. Brodie and C.A. Spindt, “Vacuum Microelectronics,” *Advances in Electronics and Electron Physics, Vol 83*, Advances in Electronics and Electron Physics 83, 1992, pp. 1-106.
5. C.A. Spindt, et al., “Field-emitter arrays for vacuum microelectronics,” *IEEE Transactions on Electron Devices*, vol. 38, no. 10, 1991, pp. 2355-2363.
6. J. Zhan, et al., “Synthesis and Field-Emission Properties of Ga_2O_3-C Nanocables,” *Chem. Mater.*, vol. 16, no. 24, 2004, pp. 5158-5161.
7. C.B. Cao, et al., “Growth and field emission properties of cactus-like gallium oxide nanostructures,” *Journal of Physical Chemistry C*, vol. 112, no. 1, 2008, pp. 95-98.
8. Y.C. Choi, et al., “Catalytic Growth of β-Ga_2O_3 Nanowires by Arc Discharge,” *Advanced Materials*, vol. 12, no. 10, 2000, pp. 746-750.
9. K.C. Lo, et al., “Preparation of GaN thin film and Ga_2O_3 nanoribbons by plasma immersion ion implantation of N into GaAs,” *Journal of Applied Physics*, vol. 95, no. 12, 2004, pp. 8178-8184.
10. J. Robertson and B. Falabretti, “Band offsets of high K gate oxides on high mobility semiconductors,” *Materials Science and Engineering B-Solid State Materials for Advanced Technology*, vol. 135, no. 3, 2006, pp. 267-271.
11. D. He, et al., “Electron transport and electron field emission of nanodiamond synthesized by explosive detonation,” *Diamond and Related Materials*, vol. 9, no. 9-10, 2000, pp. 1600-1603.
12. C.M. Yeh, et al., “Field emission from a composite structure consisting of vertically aligned single-walled carbon nanotubes and carbon nanocones,” *Nanotechnology*, no. 24, 2006, pp. 5930.
13. A.M. Rao, et al., “In situ-grown carbon nanotube array with excellent field emission characteristics,” *Appl Phys Lett*, vol. 76, no. 25, 2000, pp. 3813-3815.
14. D. Golberg, et al., “Structure, transport and field-emission properties of compound nanotubes: CNx vs. BNCx (x <0.1),” *Applied Physics A: Materials Science & Processing*, vol. 76, no. 4, 2003, pp. 499-507.
15. Y. Tang, et al., “An array of Eiffel-tower-shape AlN nanotips and its field emission properties,” *Appl Phys Lett*, vol. 86, no. 23, 2005, pp. 233104.
16. C.Y. Zhi, et al., “Synthesis and field-electron-emission behavior of aligned GaAs nanowires,” *Appl Phys Lett*, vol. 86, no. 21, 2005, pp. 213108-213103.
17. T. Yamashita, et al., “Electron field emission from GaN nanorod films grown on Si substrates with native silicon oxides,” *Appl Phys Lett*, vol. 86, no. 8, 2005, pp. 082109-082103.
18. Z. Zhang, et al., “NiO films consisting of vertically aligned cone-shaped NiO rods,” *Appl Phys Lett*, vol. 88, no. 3, 2006, pp. 033101-033103.
19. Y.H. Yang, et al., “Field emission of one-dimensional micro- and nanostructures of zinc oxide,” *Appl Phys Lett*, vol. 89, no. 4, 2006, pp. 043108-043103.
20. C. Cao, et al., “Growth and Field Emission Properties of Cactus-like Gallium Oxide Nanostructures,” *J. Phys. Chem. C*, vol. 112, no. 1, 2008, pp. 95-98.