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# Nanostructural characteristics of oxide-cap GaN nanotips by iodine–gallium ions etching

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ABSTRACT

GaN nanotips array was fabricated by an iodine-assist enhanced focused ions beam etching (IFIBE) via the double masks silver oxide (AgO) and gallium oxide (GaO). The function of AgO is used to protect from the elimination of GaO so as to remain GaO on GaN nanotip. The different size of silver cluster was able to assist the formation of GaN nanotips through the double mask process (AgO and GaO). After IFIBE process, the silver mask disappeared and only gallium oxide with a polycrystalline structure was left on top. Oxide-capping GaN nanotips were able to improve the field emission properties (turn-on field was 2.2 V/μm) due to the lower work function of GaN resulted from the distribution of electron existed the interface between GaN and GaO.



## 1. Introduction

GaN is a promising candidate in optoelectronic devices due to its direct wide bandgap, large exciton binding energy and large breakdown voltage [1], especially in one-dimension nanostructures which possess high surface-to-volume ratio and quantum confinement effect. Various one dimensional GaN nanostructures including, nanowires [2,3], nanorods [4,5] and nanotubes [6,7], have been researched. Apart from the various GaN nanostructures, there is a kind of nanostructure, tip or needle-structure which has attracted a great deal of interest and it can be applied in field emission [8], high resolution atomic force microscopy (AFM) tip [9] and scanning near field optical microscopy [10]. One dimensional GaN-nanostructures are intrinsically n-type semiconductor with the larger electron density than bulk GaN [11] and a one dimensional GaN nanostructure is supposed to be an excellent candidate for field emitters due to the low electron affinity of 2.7–3.3 eV. Notably, the optimum field emission can be obtained by adjusting the appropriate distance between the nanotips to avoid the shielding effect [12,13].

Fabrication methods for GaN nanotips can roughly be categorized into two kinds, top-down and bottom-up. In previous reports, Hsu et al. fabricated GaN nanotips using the electron cyclotron resonance (ECR) plasma process [14] and Dai et al. created GaN nanotips by two hot boat chemical vapor deposition [15]. Additionally, Ng et al. used selective and anisotropic etching to make GaN nanotips [16]. Nevertheless, not only the site control but also the shapes of the features were dependent on traditional photolithography [14,16]. In general, the traditional photolithography process is very complex and inconvenient due to the process which is dependent on the mask for the achievement of the transferring pattern with the fixed mask so that the area cannot be defined in real time. In order to solve the above problems, nanosphere lithography and electron beam lithography have been developed for the modulation of defined area in real time or further process. However, the former method faces the problem of line defeat, and the latter is time consuming.

This paper demonstrates a technology which is so called iodine-assist enhanced focused ion beam etching (IFIBE) with the double masks. This technique can precisely and rapidly produce GaN nanotips without recourse of lithographic techniques for the goal of saving-time. Notably, silver is used as the first mask for reacting with iodine gas to form AgI phase which protects the gallium oxide from gas-assist etching. The activity of silver is greater than gold or platinum so that silver cluster can be oxidized to form AgO cluster

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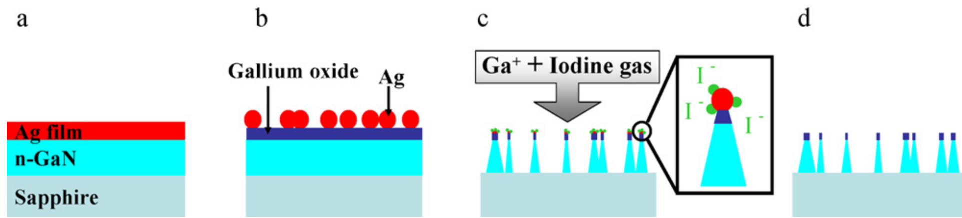


**Fig. 1.** Fabrication mechanism of GaN nanotips: (a) Ag film deposited on GaN surface by sputtering, (b) thermal treatment under 800 °C for 40 min, (c) iodine-assist enhanced focus ion beam etching process, and (d) the formation of GaN nanotip arrays with gallium oxide on top.

and then gallium oxide come after to construct as the second mask. Gallium oxides capping on GaN nanotips could improve the field emission properties.

## 2. Experiment

GaN epilayer grown on the sapphire by metalorganic chemical vapor deposition was used for the fabrication of GaN nanotips and the corresponding average carrier concentration was $8.7 \times 10^{18}$ cm$^{-3}$. The thickness of n-GaN was about 4 μm. For all experiments, the pre-clean process of the n-GaN was ultrasonically cleaned in acetone, isopropanol and hydrofluoric acid in turn and then rinsed by DI water, followed by sputtering Ag deposition on top with RF power at 40 W for 1 min and at 40 W for 5 min to obtain the two different thicknesses under a sputtering pressure of 15 mTorr. The thicknesses of Ag layers were about 10 nm and 50 nm, respectively. Then Ag/GaN with different silver thickness was annealed at 800 °C for 40 min in atmosphere using a furnace and compared to pure GaN under the same thermal treatment. In the Ag/GaN cases, the Ag film would form a single cluster for first mask formation due to the strong aggregation effect which exposed the GaN surface, while the naked GaN surface would be oxidized to form gallium oxide in a high temperature environment. Gallium oxide was used as the second mask.

At the final step, the annealed Ag/GaN and annealed n-GaN were loaded into the $Ga^+$ source focused ion beam (FIB) system for iodine-assist enhanced FIB etching (IFIBE) with a vapor pressure of 0.3 Torr for iodine at a chamber pressure of $5 \times 10^{-5}$ Torr. The Ag/GaN epilayer was etched to become a tip-like structure after IFIBE and the length of the nanotip was proportional to the thickness of the sputtered Ag film. In other words, the annealed pure GaN possessed the shortest length nanotip.

The field emission current–voltage (*I*–*V*) of the GaN nanotips was measured at room temperature under a pressure of $\sim 6 \times 10^{-6}$ Torr. Indium tin oxide (ITO) layer was used as anode and an indium layer on the un-etched GaN surface was employed to act as cathode. The distance between the anode and cathode was 180 μm and they were separated by a mica sheet. Voltage was applied up to a maximum of 1100 V to extract the electrons from the cathode so as to obtain the field emission *I*–*V* curves. In addition, the effective emission area was 100 μm$^2$, estimated by SEM geometrical measurement.

## 3. Results and discussion

The fabrication mechanism of oxide-capping GaN nanotips through three steps, deposition of silver, annealing in atmosphere and IFIBE had been demonstrated in Fig. 1. In the first step, the silver layer was deposited on the n-GaN surface by sputtering. The resulting multilayer structure is shown in Fig. 1(a). After thermal annealing in air, the silver film became an isolated cluster as the first mask as shown in Fig. 1(b) and the thermal treatment was kept intentionally at 800 °C for 40 min in order to increase the partial pressure of oxygen. Due to the aggregation of the silver film under high temperature treatment, GaN surface would be exposed to the atmosphere and followed by oxidizing, and acted as the sec-

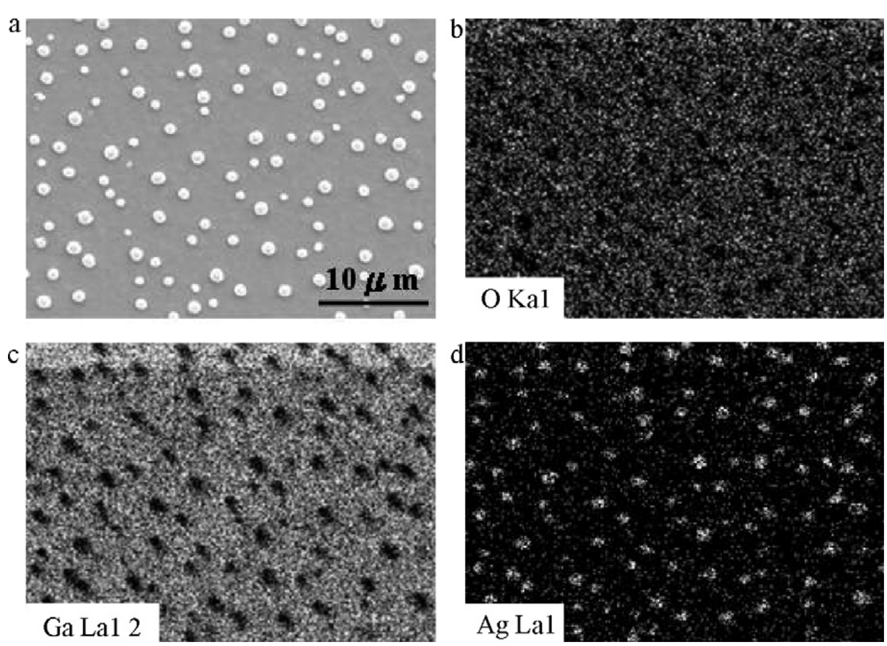


**Fig. 2.** Film surface characteristics: (a) SEM image of the partial oxidized Ag particle on n-GaN after annealed 800 °C 40 min in air and EDS mapping results of (b) O-Ka1 (c) Ga-La1_2 (d) Ag-La1 corresponding to (a).

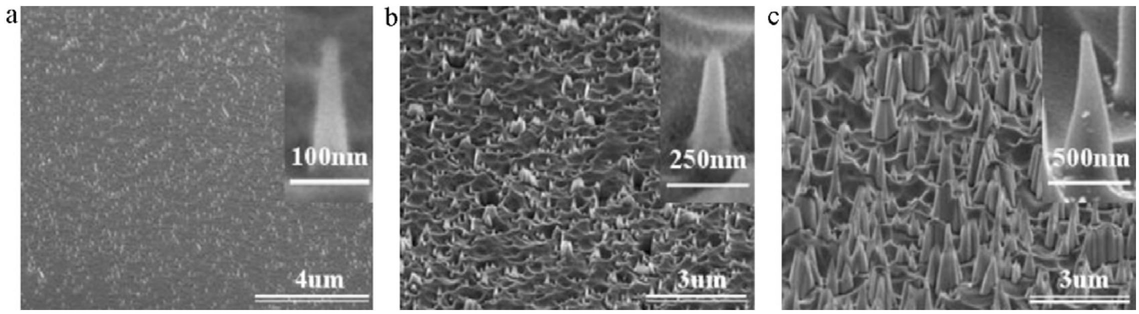


**Fig. 3.** Typical SEM image of GaN nanotips fabricated by enhanced focus ion beam etching in the presence of iodine ambient (a) without silver mask, (b) with 10 nm silver thickness, and (c) with 50 nm silver thickness.

ond mask. The silver cluster also partially oxidized to form silver oxide at 800 °C. According to free energy [17,18], AgO will partially reduce to form Ag, and GaN will oxidize with O to form GaO on GaN. The main reason is that gallium oxides still appear in the interface between GaN and AgO. Meanwhile, $Ga^+$ and iodine gas are responsible for the physical etching and chemical etching. AgO cluster and gallium oxide on GaN surface acted as double masks against etching as shown in Fig. 1(c). It is interesting to look into the behavior of the silver clusters which reacted with iodine gas and there are two reactions between the silver or AgO clusters and the iodine. In the first one, the silver cluster part adsorbed the iodine gas, preventing the iodine gas from touching the sample surface to perform dry etching. In another one, the iodine gas reacted with the AgO cluster and the chemical reaction is $2AgO_{[S]} + 2I_{[G]} \rightarrow AgI_{[S]} + O_2\uparrow$. GaN nanotips with gallium oxide on top eventually formed as shown in Fig. 1(d) and AgO cluster would gradually become small to disappear during the dry etching process.

After the Ag film formed the AgO clusters, naked GaN surface oxidized to produce the second mask and the morphology is shown in Fig. 2(a). Energy dispersive spectrometer (EDS) mapping images of the annealed Ag cluster are shown in Fig. 2(b)–(d). Notably, the film surface was almost oxidized but the parts of Ag clusters were not oxidized, as shown in Fig. 2(b). There are no Ga ions diffused into the Ag/AgO clusters (Fig. 2(c) and (d)).

Fig. 3 shows the typical tilted view of GaN nanotips by the IFIBE technique using scanning electron microscope (SEM) and the insets in the upper right-hand corner are magnified images of GaN nanotips through the single and double mask shelters. The diameter of GaN nanotip is about 50 nm in Fig. 3(a) and GaN nanotips with different oxide-capping are about 125 nm and 250 nm, as shown in Fig. 3(b) and (c), respectively. GaN nanotips were observed to be aligned and distributed in the defined area. Similar geometric morphologies of GaN tip-structures are seen in Fig. 3.

Further structural investigation was carried out using a transmission electron microscope (TEM). The typical HRTEM images of oxide-capping GaN nanotip (Ag: 50 nm) created by IFIBE through the double mask process are shown in Fig. 4. In Fig. 4(a), a GaN tip-structure with GaO on top is observed and the height of the gallium

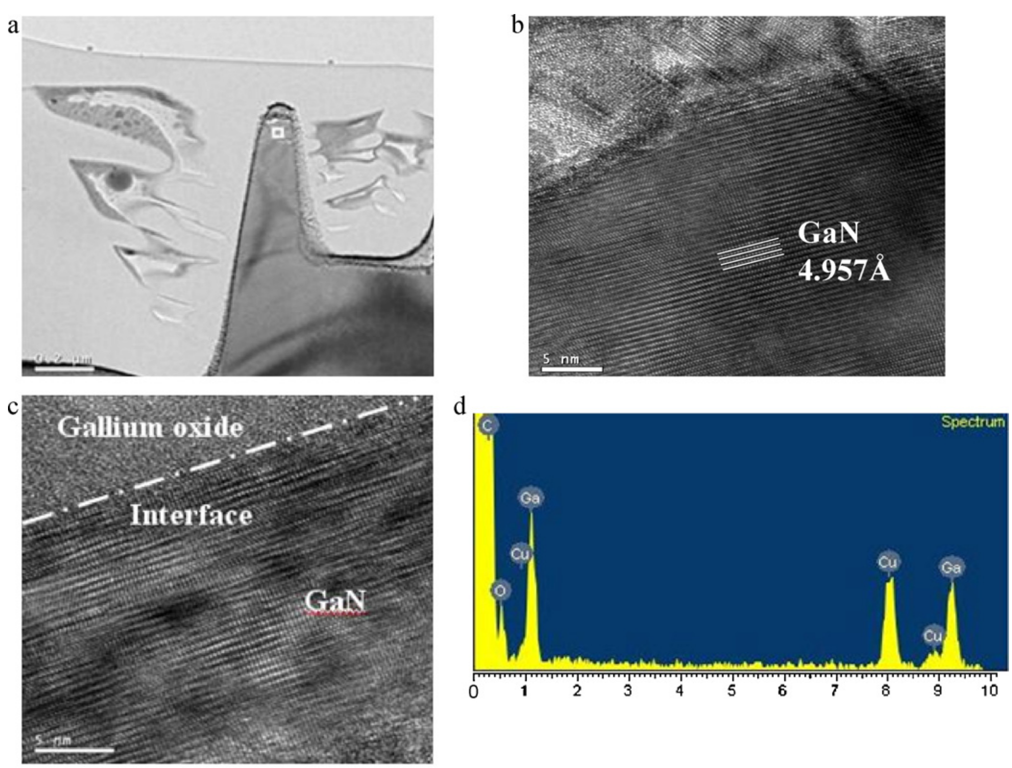


**Fig. 4.** TEM images of Ag/GaN nanotips fabricated by iodine-assisted enhanced FIB etching: (a) cross section image, (b) high resolution of GaN nanotip body (magnified view white square in Fig. 3(a)), (c) interface between GaN nanotips and gallium oxide, and (d) EDS of gallium oxide.

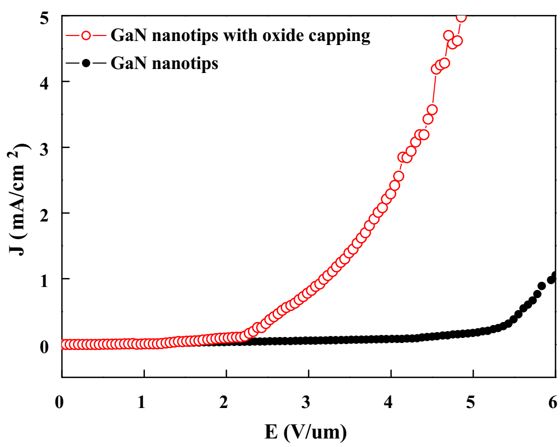


**Fig. 5.** Comparison of field emission current density-electric field ($J$–$E$) curves of oxide-capping GaN nanotips and GaN nanotips.

oxide on GaN nanotip is about tens nm. The detailed characteristics of the GaN nanotip body and the interface between the GaN nanotip and GaO are shown in Fig. 4(b) and (c) as well as the lattice spacing of GaN of 4.957 Å. From Fig. 4(c), the interface can be clearly distinguished and gallium oxide is a poly-crystalline structure. The top particle is gallium oxide and the corresponding energy dispersive spectrometer (EDS) is shown in Fig. 4(d) and only gallium oxide was detected (without Ag signal). Therefore, partial oxidized silver cluster was used to protect the gallium oxide from over etching so as to keep the gallium oxide on the GaN nanotips top for enhancement of field emission property.

In Fig. 4, no AgO cluster could be seen on the top of the GaN nanotips. The fabrication of GaN nanotips without oxide-capping was utilized GaO as the mask. Basically, GaN nanotips without oxide-capping have the shortest length due to free of AgO shelter. It means that the different silver thicknesses had produced the different lengths of GaN nanotips. The main function of silver is used to prevent gallium oxide and assist the development of oxide-capping GaN nanotips. However, the lengths of GaN nanotips without the silver masks were all below 200 nm. In the as-deposited 10 nm silver layer case, the length of GaN nanotips ranged from 200 nm to 1000 nm. In the as-deposited 50 nm silver thickness case, the GaN nanotips were longer and ranged from 800 nm to 1000 nm.

Herein, we pick up GaN nanotip and oxide-capping GaN nanotips (50 nm Ag thickness) for the field emission measurement. The field emission property of GaN nanotips compared to oxide-capping GaN nanotips are shown in Fig. 5. The turn-on field ($E_T$) was chosen as the applied electric field for 0.1 mA/cm$^2$ current density. The measured $E_T$ was 4.3 V/μm for the n-GaN nanotips without gallium oxide. For the 50 nm case of Ag/GaN nanotips with gallium oxide capping, the $E_T$ was 2.2 V/μm. The oxide capping on the GaN nanotips caused an obvious improvement in field emission. In general, the electric field intensity was stronger at the top of the tip-like structure. Additionally, the formation of an interface between the gallium oxide and GaN promoted a charge redistribution of GaN atoms on the side of GaN. Tang et al. demonstrated that $Ga_2O_3$ decorated on GaN nanowires could be used to improve the field emission property [19]. In the present experiment, gallium oxide only existed on the top of GaN nanotips so that the charge redistribution was focused at the top of the nanotip and further reinforced the field emission. In other words, the effect had reduced the effective work function and this is the main reason that the array of GaN nanotips increased the emitted electron concentration. The values of $E_T$ in both present cases were almost the same as theirs. Notably, the better value of $E_T$ (Fig. 5) can be ascribed to the appropriate number of nanotips without the presupposition of the screen effect and the inherently high carrier concentration [20]. The Ag/GaN nanotips fabricated by IFIBE can be used to enhance the field emission property.

## 4. Conclusion

In summary, an array of GaN nanotips is fabricated successfully using iodine-assist enhanced focus ion beam etching (IFIBE). The lengths of the Ag/GaN nanotips increase when the thickness of the sputtered silver film is increased. During IFIBE process, Ag masks protect the gallium oxides from being etched badly and the field emission property is improved by oxide covering the GaN nanotips.

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