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Fabrication of GaN Nanocone Arrays on Si by Pulsed Laser Ablation using Anodic Aluminum Oxide Mask

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We demonstrate the fabrication of Gallium Nitride (GaN) nanocone arrays of different heights on Si by pulsed laser deposition using an Anodic Aluminum Oxide (AAO) as a mask. A highly self-ordered hexagonal array of cylindrical pores has been fabricated by anodizing a thin film of Al on substrate and subsequent growth of GaN into these nanoholes has been performed by pulsed laser ablation. Arrays of nanocones were examined under the field emission Scanning Electron Microscopy (SEM). The height of these nanocones is also observed to be affected by the change in target to substrate distance and laser fluence. X-ray Photoelectron Spectrum (XPS) is obtained to confirm that these are GaN nanocones. X-ray diffraction (XRD) spectrum is also obtained to examine the crystal structure of these nanocones. In addition, a simple method to strip off the AAO template after synthesis is also used. This technique of stripping off the template is hassle-free compared to the conventional wet-etching method. AAO template-based synthesis method provides a low cost process to fabricate GaN-based nanomaterials fabrication.

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1. Introduction

The fabrication of pseudo-regular arrays of nanostructures has attracted considerable interest due to their potential nanodevice applications such as optoelectronics, information storage, and sensors [1-3]. Several methods have been employed to produce arrays of nano-structures, including lithographic techniques [4, 5], deposition of materials onto self-ordered surfaces [6], controlled nanoparticle growth by diffusion [7], self-assembly of nanoparticles from solution onto substrates [8], and template-based methods [9].

A method which entails synthesizing the desired material within the pores of a nanoporous membrane is called “template synthesis” [10]. In this case, the size and shape of the nano-structures are controlled by the size and shape of the openings of the nanotemplates. One of the attractive templates is AAO. AAO film, which has ordered pores of dimensions ranging from the submicrometer to nanometer range, has recently attracted much attention because of the usage of a host or template for the fabrication of nanodevices such as electronic, optoelectronic, and micromechanical devices [11-13]. AAO is known for more than 50 years but only in 1995, it was observed that ordered arrays of porous aluminum oxide could be obtained for nanofabrication [14]. The geometry of anodic porous aluminum may be schematically represented as a honeycomb structure with a high aspect ratio (depth divided by width) of fine channels characterized by a close-packed array of columnar hexagonal cells, each containing a central pore, as shown in Fig. 1 [14].

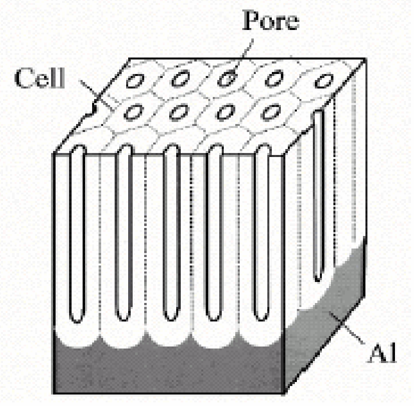


Fig. 1 Schematic drawing of the structure of anodic porous aluminum oxide.

The template method has a number of interesting and useful features. It can be used to prepare conductive polymers, metals, semiconductors, carbon tube and other materials. Furthermore, nanostructures with extraordinarily small diameters which are too small to be made with the lithographic methods can be prepared. The diameters of the hole can also be easily controlled through external conditions such as acid concentration and applied voltage.

AAO films possess pseudo-regular and highly anisotropic porous structures with pore diameters ranging from 10 to 200 nm, pore length from 1 to 50 μm, and pore densities in the range 10^9-10^{11} cm^{-2}. The pores have been found to be uniform and nearly parallel, making the AAO films ideal templates for the deposition of nanometer-scale particles. The AAO template also allows one to manipulate the nano-structure arrays and to incorporate them into a variety of potential designs of nano-devices.

To date, there have been no reports on fabrication of GaN nanocones using AAO and pulsed laser ablation. Here, we demonstrate that pulsed laser ablation can be applied to deposit semiconductor nanocones of different heights onto Si using AAO nanotemplate as a mask. The morphology, heights variation, binding energy and crystallinity of the fabricated nanocones are studied. In addition, we demonstrate an easy method of stripping off the AAO template after fabrication which is hassle-free compared to the conventional wet-etching method.

2. Experimental Procedure

2.1 Template Fabrication

Anodization was conducted under constant cell potential in aqueous solution as electrolyte. The sample with Al deposited on the substrate was mounted on a copper plate serving as anode and exposed to the acid in a thermally isolated electrochemical cell (Fig. 2). During anodization, the electrolyte was stirred.

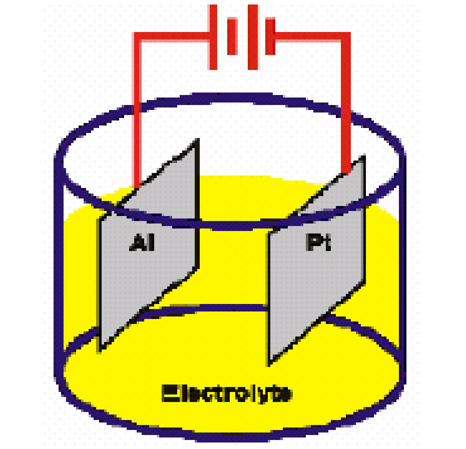
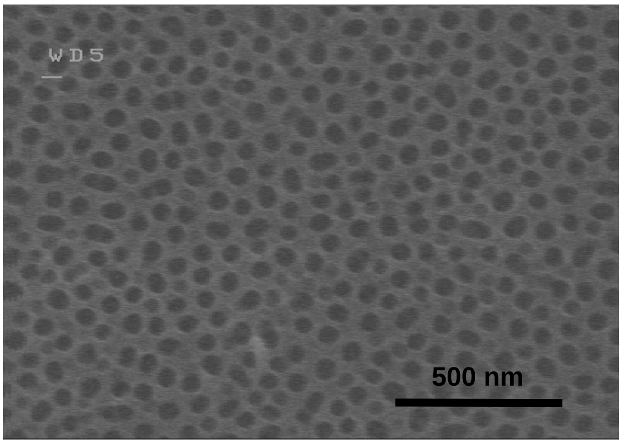


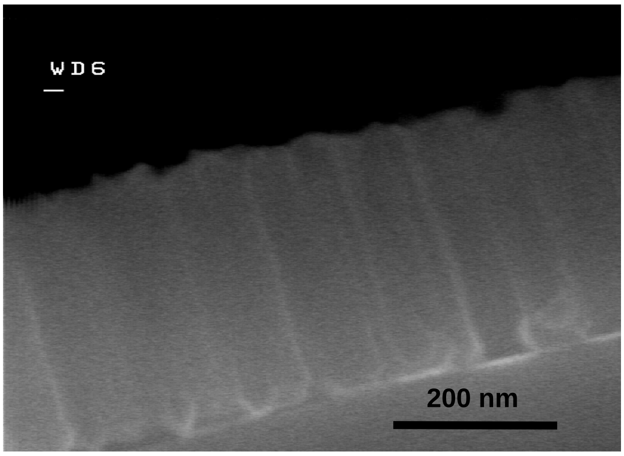
Fig. 2 Schematic equipment of anodization.

In this work, 400 nm thick of aluminium (Al) film is deposited on the substrate by an e-beam evaporator. This film is then used to fabricate the AAO template rather than by anodizing Al using bulk or thin sheets of Al. Tedious procedures that limit the templates' practicality are thus avoided [15, 16]. The process steps used in the fabrication of the AAO are described as follows. A two-step anodizing process reported by Masuda [14] was employed. The e-beam deposited Al film is first anodized at the voltage of 40 V in 0.3 M oxalic acid solution at about 4 °C. Then the anodized layer, which covers the top part of the film, is removed in a mixture of phosphoric acid (H_3PO_4) and chromic acid. The textured Al plate was anodized again under the same condition as the first. The second anodization step lasted until the Al film has been completely converted to an AAO film. Subsequently, the samples were dipped in 5 wt% H_3PO_4 at room temperature for 45 minutes to remove the thin barrier layer. The pore diameter can be increased by an additional pore widening etch.

Figure 3 shows the SEM image of the AAO. We confirm the nanoholes with relative uniform pores structure are arranged with relative regularity. The mean diameter of the holes as measured from the SEM was about 50 nm. The cross-sectional view of SEM shows that the holes were cylindrically parallel and non-intercepting. The thickness of the template is about 300 nm.



(a)



(b)

Fig. 3 SEM images of (a) top view and (b) cross-sectional view of an AAO template.

2.2 Pulsed laser ablation fabrication of GaN nanocones

GaN nanocones were fabricated in a vacuum chamber using pulsed laser ablation on AAO template (Fig. 4). The target was first prepared using GaN powder (99.99+ % purity, Aldrich) pressed into a solid tablet at a pressure of 10 MPa. It was then loaded into the chamber and held by a rotating target holder. Silicon substrates, with AAO template on top, were placed on a substrate holder which was positioned opposite the GaN target. After evacuating the chamber to a base pressure of 1.5 x 10^{-4} mbar, laser beam was focused onto the rotating GaN target to perform the laser ablation. The laser used in this process is Nd:YAG laser (λ = 532 nm, pulse repetition rate = 10 Hz). The morphology and crystal structure of the nanocones grown were examined with field emission SEM (Hitachi S4100). The binding energy of these GaN nanocones is also determined using XPS while XRD is used to examine the crystallinity of these nanocones.

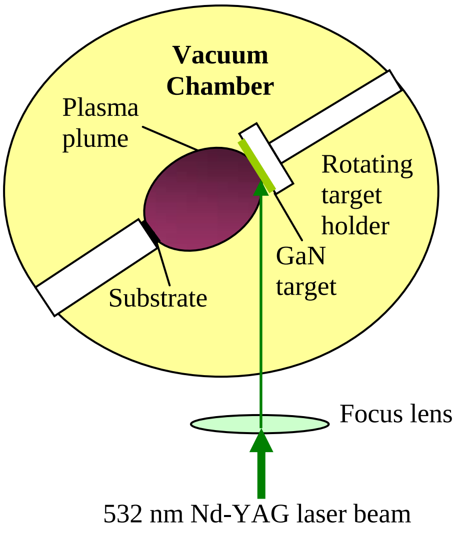


Fig. 4 Schematic drawing of experimental setup of pulsed laser ablation fabrication of nanocones.

3. Results and Discussion

3.1 Characterization of the GaN nanocones

The morphology of the nanocones fabricated is observed under the SEM. Figure 5 shows an array of well-aligned nanocones formed after pulsed laser ablation. The base diameter of each nanocone is around 50 nm (following that of the diameter of each nanopore) with the tip being sharp.

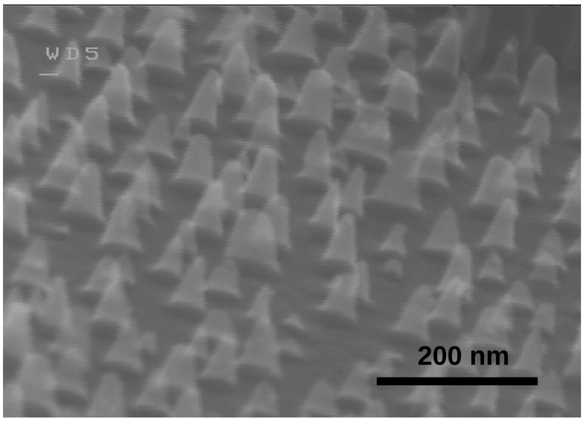


Fig. 5 SEM image of the nanocones fabricated by pulsed laser ablation.

XPS studies using monochromatic Al K-alpha X-ray source was also carried out to confirm the bonding of GaN. From the narrow scan of the Ga2p$_{3/2}$ core-level spectrum of the nanocones in Fig. 6, the binding energy of the Ga-N bonds is found to be 1117 eV, which is as presented by Lin et. al.[17]. Furthermore, a binding energy of 1117 eV, and with both Ga and N being present, suggests that the Ga and N atoms are held together by a common binding energy, thus indicating the formation of GaN.

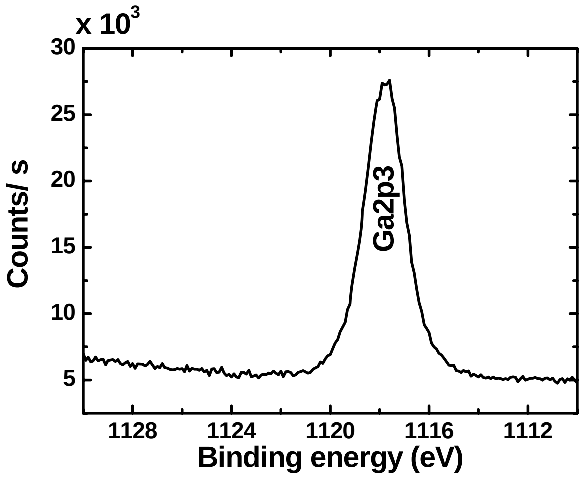


Fig. 6 XPS spectrum of the GaN nanocones showing its binding energy at 1117 eV.

Figure 7 shows the X-Ray Diffraction (XRD) spectrum of these nanocones. The spectrum obtained showed that these nanocones are generally amorphous. This amorphous nature could be due to the fact that no heat treatment is performed during the synthesis.

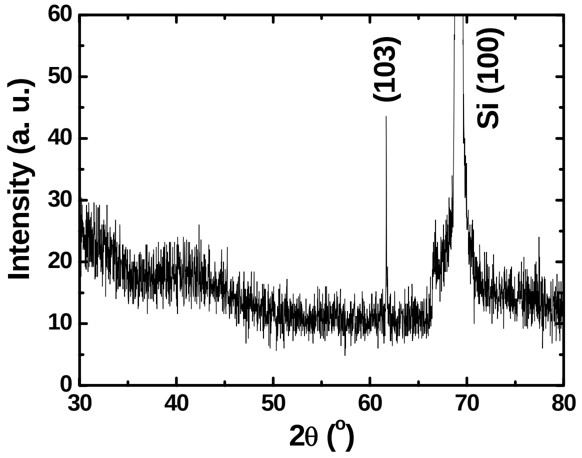
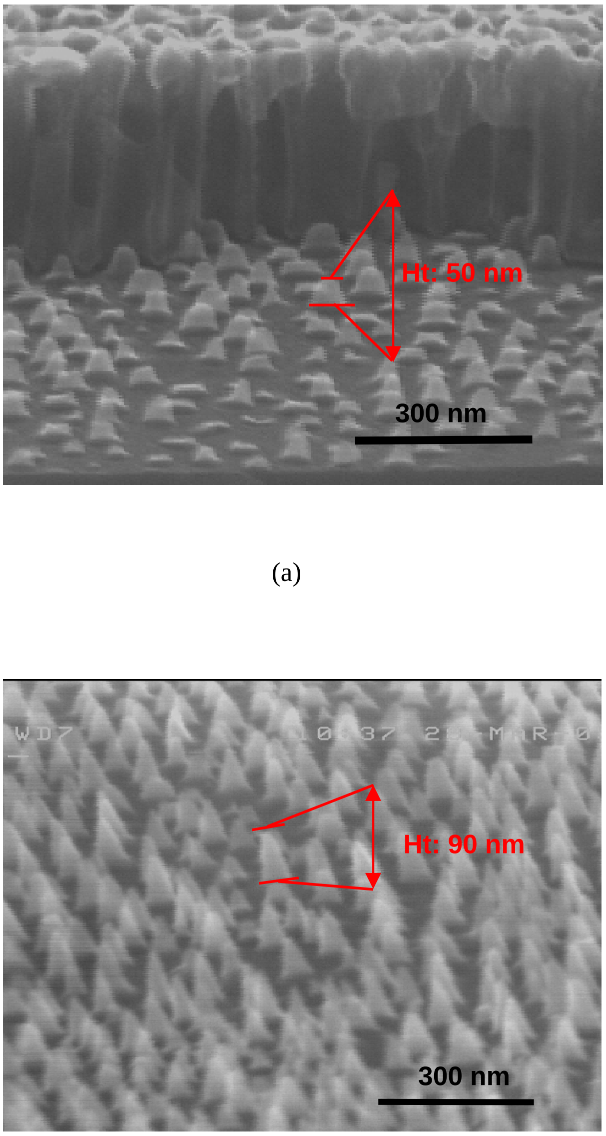


Fig. 7 XRD spectrum obtained for the nanocones.

3.2 Changing the target to substrate distance

Figure 8 shows the SEM images of the nanocones fabricated by pulsed laser ablation at different target to substrate distances with laser fluence = 4.3 J/cm^2. The SEM images show that the height of the nanocones increases with target to substrate distance. The reason being as the target to substrate distance increases, the particles of the GaN flux from the plasma plume caused by laser ablation becomes smaller and thus, enter the nanopores more easily.



(a)

(b)

Fig. 8 SEM image of nanocones fabricated at target to substrate distances of (a) 9 cm and (b) 12 cm.

3.3 Changing the laser fluence

The laser energy was then reduced laser fluence = 1.83 J/cm^2 while maintaining the longest initial target to substrate distance of 12 cm and the nanocones continue to have maintain its longer height of 90 nm (Fig. 9). Further reduction in laser fluence = 1.43 J/cm^2, however, does not yield further results (Fig. 10). Therefore, we deduced that there will come a point when the reduction in laser energy no longer increases the height of the nanocones. Laser fluence = 1.83 J/cm^2 is concluded to be the saturation laser energy point for the increase in the height of the nanocones.

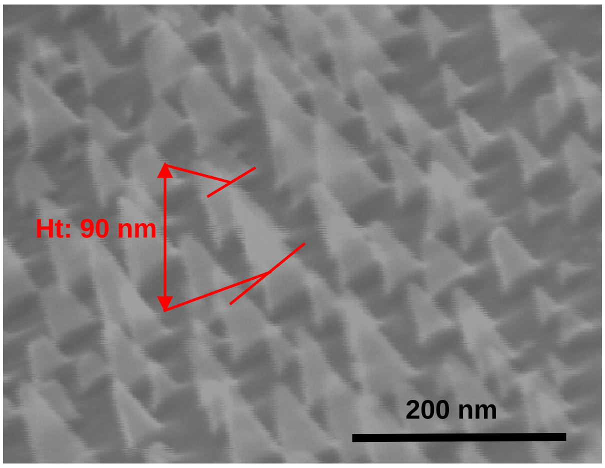


Fig. 9 SEM image of nanocones fabricated when laser fluence is reduced to 1.83 J/cm^2.

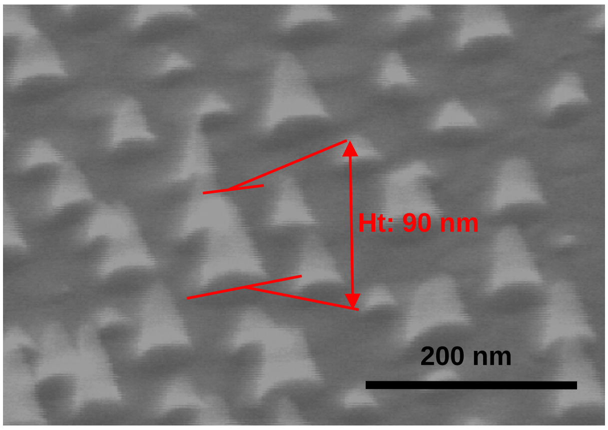
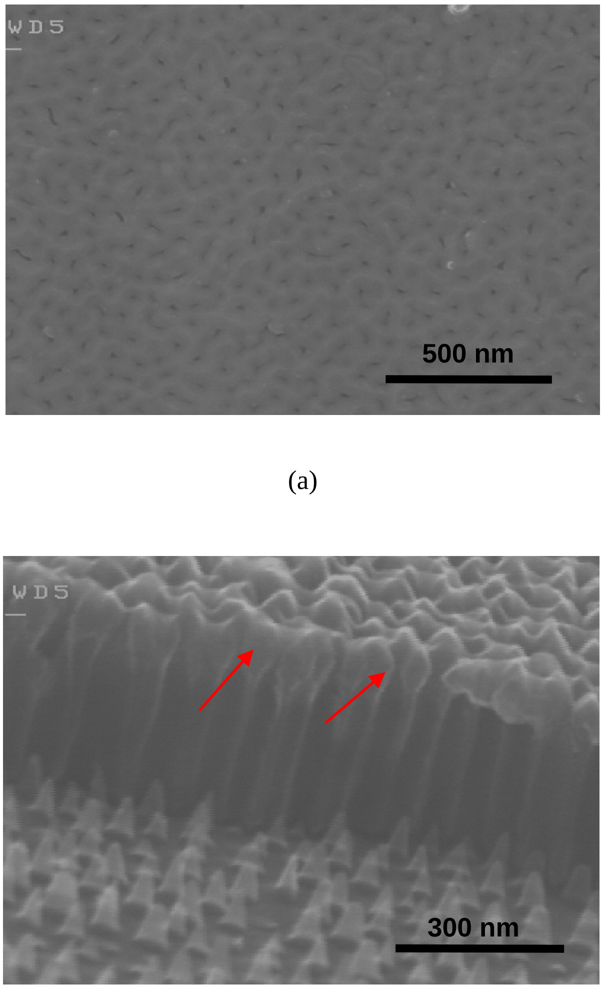


Fig. 10 SEM image of nanocones fabricated with further reduction of laser fluence to 1.43 J/cm^2.

3.4 Saturation of nanocones heights

Figure 11 further shows the height of the nanocones saturating at each target to substrate distance. Once the top of the nanopores are filled up by the GaN flux from pulsed laser ablation, the height of the nanocones will terminate at a point as no more GaN flux can enter the nanopores.

This problem may be solved by using laser to ablate the surface of the AAO template during synthesis to maintain the opening of the nanopores. However, this proposed solution needs to be further developed experimentally.



(a)

(b)

Fig. 11 SEM images showing (a) top and (b) cross-sectional view of the AAO template after pulsed laser ablation. The arrows show the regions where the nanopores are ‘clogged’.

3.5 Removing AAO template

The AAO template was removed after pulsed laser ablation to obtain the pseudo-regular arrays of nanocone. The conventional way of template removal is by chemical etching [18] which normally result in most of the nanocones falling off the substrate. Figure 12 shows the few remaining nanocones after immersing the AAO template after pulsed laser ablation for 1 min in 1 mol of sodium hydroxide (NaOH). The few nanocones left will not allow for further application.

Here, we used a simple way of removing AAO template. The template is removed by sticking scotch tape on the surface of the template and pulling them off. As the AAO template forms a thin layer on the surface of the Si substrate, the scotch tape, when adheres well on the surface of the AAO, can cause the template to be stripped off when the scotch tape is removed. Whatever remains on the Si substrate are the arrays of nanocone. This method is simple and hassle-free compared to the wet-etching method. Figure 13 shows a low magnification of the arrays of nanocone after stripping off the template using the scotch tape. In addition, as there is no heat or electrical treatment during the synthesis of these nanocones, the nanocones adhesion forces to the Si substrate are weak. The use of scotch tape to remove the AAO template will cause less disruption to the nanocone-substrate interface compared to the wet-etching method. Hence, more arrays of nanocone are left behind on the substrate after template removal.

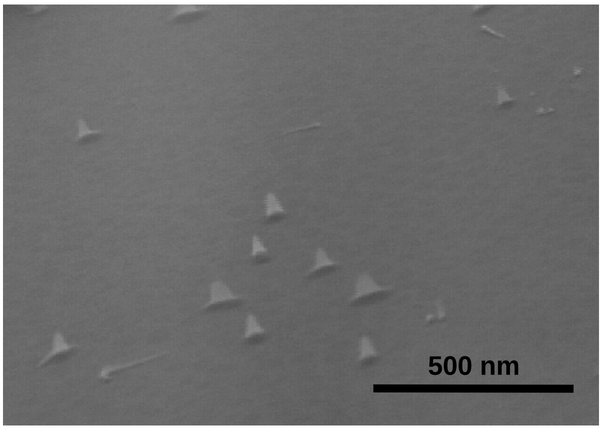


Fig. 12 SEM image of few nanocones that remained after stripping off the AAO template using wet-etching.

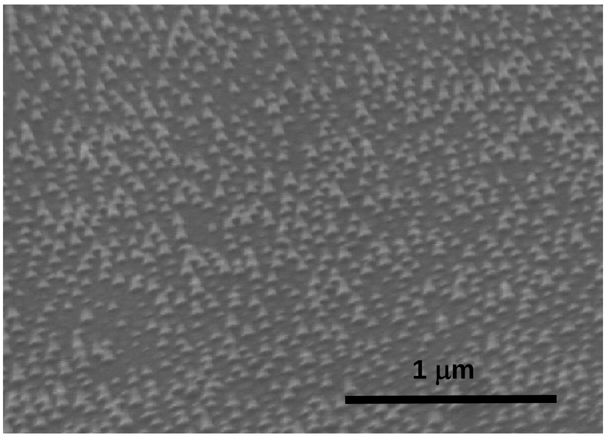


Fig. 13 Low magnification SEM image of remaining nanocones after stripping the template with scotch tape.

4. Conclusion

Pseudo-regular arrays of GaN nanocone are fabricated using pulsed laser ablation with AAO templates to regulate their diameters. The heights of the nanocones are examined using field emission SEM while varying the target to substrate position and the laser energy. A simple method of stripping off the AAO template after fabrication of the nanocones is also demostrated.

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