ORDERED GaN AND InGaN NANOSTRUCTURES FABRICATED USING NANOSPHERE LITHOGRAPHY TECHNIQUES

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Abstract

Lithography is an important step during fabrication of the ordered nanostructures. To process large area, the selected fabrication method should have high throughput, while also being low-cost, this can be achieved by employing nanosphere lithography (NSL). The main idea of NSL, is to deposit single layer of spheres, which serves as a mask, through which the final nanostructure is etched out. The aim of this work is to demonstrate that NSL is a viable technique to fabricate GaN and InGaN triangular nanostructures as well as nanowires. Whole fabrication process consists of deposition of the polystyrene spheres, metal deposition to cover the whole sample and spheres lift-off to expose the material beneath. In the final step $SiCl_4$/Ar plasma was used to finalize the triangular nanostructure, which can be further etched in an etchant to produce nanowires. It is necessary that for each step the optimal parameters are found to achieve reliable reproducibility. Whole fabrication process shall be characterized by electron microscope, cathodoluminescence spectroscopy and Energy-dispersive X-ray spectroscopy. Resulting nanostructures should have large surface area, which should be advantageous for applications in photocatalytic water splitting and other various applications depending on the material selected.

Keywords: Nanosphere lithography, Gallium nitride, Nanostructures

1. INTRODUCTION

In recent years, the demand for smaller and more efficient materials has been steadily increasing. Fabrication of such materials can be broadly categorized into two main approaches Top-down and bottom-up. Top-down techniques utilize lithography or milling to create a nanostructure from a bulk material or a thick layer, in case of bottom-up approach a nanostructure is grown from a precursor atoms and molecules that self-assemble. For certain materials or a nanostructure only one approach could be used such as indium gallium nitride ($In_{(x)}Ga_{(1-x)}N$), a semiconductor with tunable bandgap from 3,4 eV for x = 0 to 0,65 eV for x = 1. The ability to influence the band gap by changing In fraction is an essential property that could lead toward the development of a photocatalytic nanostructure for water splitting [1]. Such a structure should have a large surface area, which is an important parameter when the efficiency of a material is proportionate to its active surface. Currently, it is still a challenge to prepare InGaN nanorods or any other structure with large surface using bottom-up approach, however it is possible to grow a thick InGaN layer and then to use lithography to produce the desired structure.

Standard lithography methods have been successfully used for fabrication of nanostructures; methods such as electron beam lithography and focused ion beam milling can be used to fabricate structures with complex geometries down to a size of 10 nm. However, these methods have several drawbacks that prevent large-scale production, such as expensive equipment and high operating cost, while offering low throughput. Nanosphere lithography is a group of techniques that are low cost, with high throughput, that allow for fabrication of 2D/3D nanostructures [2]. The fundamental limitations are the resolution and configuration of the

prepared structures, which are due to the use of a close-packed hexagonal self-assembled monolayer as a mask. The mask itself is usually made of polystyrene (PS) or silica (SiO_2) spheres of uniform diameter.

There have been reported many different strategies to produce defect-free monolayers. Spin coating involves dropping a colloidal suspension onto a hydrophilic substrate, followed by an accelerated evaporation process in a spin coater. Precise control of the spin rotation, acceleration, the size and the concentration of spheres, and the substrate wettability is crucial for successful fabrication. Due to the large number of parameters, the right setting is usually found empirically. Another method called drop coating, involves dropping a drop of solution onto the substrate and subsequently allowing for the solvent to evaporate. Although the method is very simple, it does not offer a great degree of control. Monolayers can be also prepared by method called water-air interface (WAI), that follows a different approach. Instead of forming a monolayer directly onto the surface, the monolayer is formed on the surface of a liquid. Before the monolayer formation, a substrate is placed below the liquid surface, which is then lifted from the liquid with trapped spheres onto it. With precise control, it is possible to transfer the monolayer from the liquid surface to the substrate [3]. Subsequently deposited spheres are covered by a metallic layer to protect the area between the spheres. After the sphere lift-off, the material under the sphere is left exposed, which is then etched out in a specific plasma. The resulting nanostructure is created in a place that was protected by the metallic layer. In the final step, the metallic layer is removed, typically by wet etching. The whole fabrication process can be seen in **Figure 1**.[3]

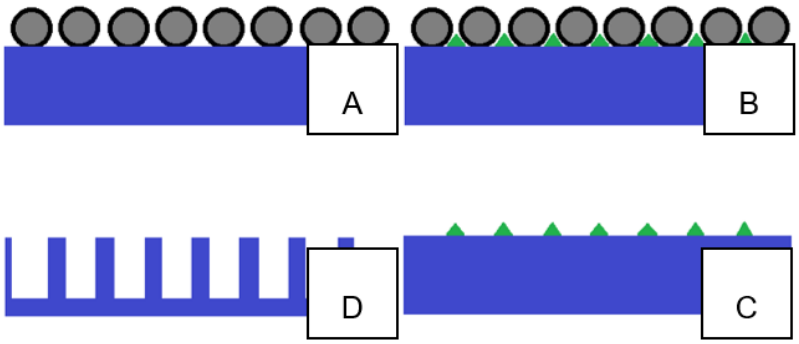

Figure 1 NSL scheme; Sphere deposition (A), Metallic coating (B), Sphere lift-off (C), Plasma etching (D)

2. MATERIAL AND METHODS

A 2,5 wt % monodisperse polystyrene sphere water solution with diameter 2 μm was bought from the AliExpress. Sodium dodecyl sulfate (SDS) and cyclohexanone were purchased from Sigma-Aldrich. Ethanol, Acetone were purchased from P-Lab.

All samples used in this study were prepared by metal organic vapor phase epitaxy (MOVPE) on c-oriented sapphire substrates using an Aixtron 3 × 2” CCS MOVPE system, equipped with LayTec EpiCurveTT in situ monitoring. For the growth of GaN and InGaN layers, trimethylgallium (TMGa), trimethylindium (TMIn), and ammonia (NH_3) precursors were used, always in an H_2 atmosphere. The prepared substrate was cut into 10 × 10 mm samples or larger. All samples were characterized by scanning electron microscope (SEM) Philips 30 XL equipped with an energy-dispersive X-ray spectroscopy (EDX) probe and a cathodoluminescence (CL) detection system, or by SEM Tescan MAIA.

Before nanosphere deposition, the substrate was cleaned in acetone, ethanol, and deionized water, each for 10 minutes in ultrasonic bath, totaling 30 minutes. To turn the substrate hydrophilic an oxygen plasma was used for 120 seconds [4]. For each method used a different solution of nanospheres was prepared. For the spin coating, a 50 μL droplet of polystyrene spheres in water solution was deposited onto the substrate and spun for 30 seconds using spin speeds of 1000 and 7000 rpm. The PS: water ratios used were 5:1000, 10:1000, 20:1000, and 30:1000. In case of drop coating, a drop of solution with volume from 10 to 25 μL was

dropped unto the surface and left to evaporate. The solution consisted of 500 µL (30:1000 PS: water) PS solution mixed with 500 µL ethanol. Additionally, 100 µL of SDS solution (c = 1,7335 mM) was added to promote self-assembly of the nanospheres. The water-air interface experiments were conducted in the Petri dish, in which the substrate was submerged. Several drops of SDS (2% wt) were added before a glass slide was positioned at a 40° angle in the Petri dish [3]. Solution was pipetted onto the glass slide. As the solution contacted the water surface, a thin layer of polystyrene developed onto the water surface (**Figure 2B**), the amount of solution depends on the size of a sample. The PS solution consisted of (1:1) PS mixed with ethanol. After monolayer formation, the liquid was slowly drained by a syringe. To improve the formation of the monolayer, the area was confined to area slightly larger than the sample itself (**Figure 2C**).

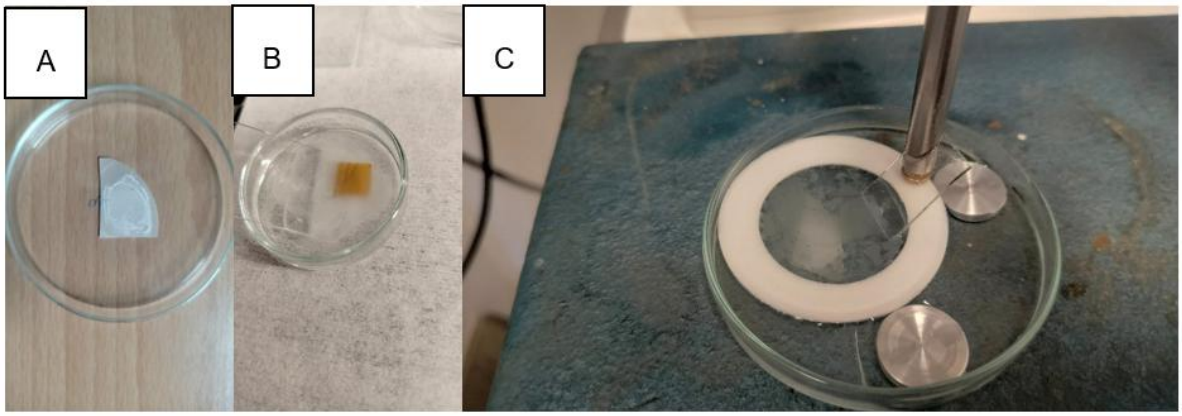

Figure 2 Experimental setup; Drop coating after liquid evaporation (A), developing sphere monolayer on the surface of the liquid using WAI (B), WAI with confined area (C)

Samples that had sufficient monolayer coverage were covered by a chrome layer with thickness 50 or 100 nm [2]. Later a Ti adhesion layer with thickness 10 nm was added. The metal layers were deposited by the thermal evaporation in the Edwards AUTO 500 chamber. The next step in the fabrication was to remove the spheres from the sample surface. To remove the spheres a combination of ethanol and mild ultrasonic sonification was used for 30 seconds. It is also possible to dissolve the PS spheres in cyclohexanone with few ultrasonic pulses. To etch the exposed areas $SiCl_4$/Ar inductively coupled plasma (ICP) was used in the Oxford Plasmalab System 100. The etching parameters were kept the same for all samples. The chosen parameters were $SiCl_4$/Ar (75/45 sccm), 20 mTorr, RF power 75 W and power ICP 45 W for 5–10 minutes. [5].

3. RESULTS AND DISCUSSION

3.1 NSL techniques comparison

From the SEM image (**Figure 3**), it is apparent that different methods yielded different layer compositions. Spin coating with our chosen parameters did not produce a compact monolayer. The spheres were loosely deposited, and large aggregates were formed (**Figure 3A**). The drop coating approach did not yield a monolayer either. The surface coverage was larger than in the case of spin coating. However, an undesirable multilayer was formed (**Figure 3B**). Also, if larger amount of PS solution was dropped, a so-called coffee ring was developed on the sample (**Figure 2A**). The water-air interface method appears to be the most promising method. Considering the layer quality, it is a monolayer with a few spots, where the spheres are arranged in the second layer (**Figure 3C**). The addition of the right amount of SDS significantly improved the monolayer quality, which enabled PS spheres deposition onto samples up to 1 cm^2, also the spheres self-arranged into the close hexagonal grid (**Figure 3D**). Therefore, the water-air interface method was chosen for further experiments.

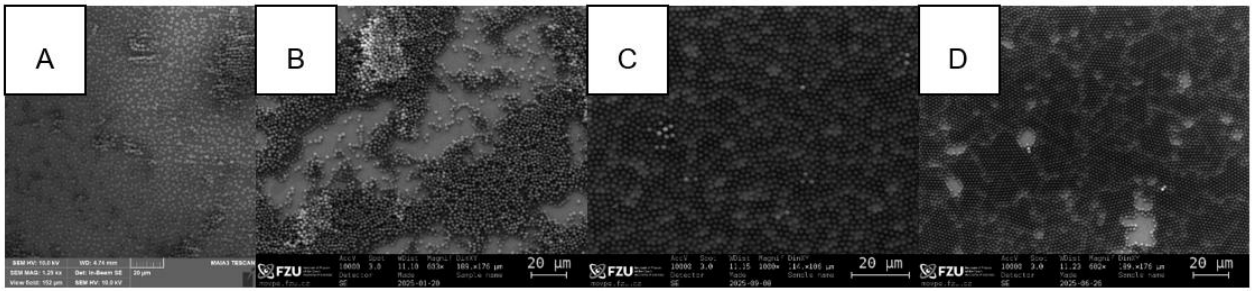

Figure 3 Comparison of deposition method; Spin coating (A), Drop coating (B), WAI (C), WAI with close hexagonal arrangement (D)

3.2 Comparison between GaN and InGaN

The final heterostructure is intended to be made of InGaN, however it is more difficult to fabricate such layer. To assess whether the choice of substrate affects the nanosphere deposition process, a comparative test was conducted using both GaN and InGaN substrates. From the SEM image (**Figure 4**), it is apparent that there are no significant differences between the PS layer on GaN and InGaN.

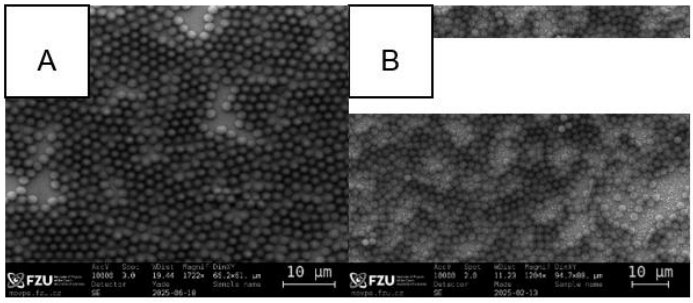

Figure 4 Comparison between GaN and InGan using WAI with the same parameter; GaN (A), InGaN (B)

3.3 Metal deposition

Due to its resistance to plasma etching, chromium was chosen as a protective layer. Therefore, a chromium protection layer with a thickness of 50 and 100 nm was deposited. The thinner layer exhibited small tears that were not presented with the thicker layer (**Figure 5A**). Also, with the thinner layer, the area in close proximity to the spheres was not covered by Cr as seen from the CL measurement (**Figure 5B**). To improve the Cr layer quality a 10 nm adhesion layer was first deposited on the sample. The presence of leftover SDS was causing weak adhesion of the metallic layer, this problem was solved by cleaning samples before the deposition in pure water for 5 minutes multiple times. With the cleaning step and addition of Ti layer, a defect free layer was deposited (**Figure 5C**).

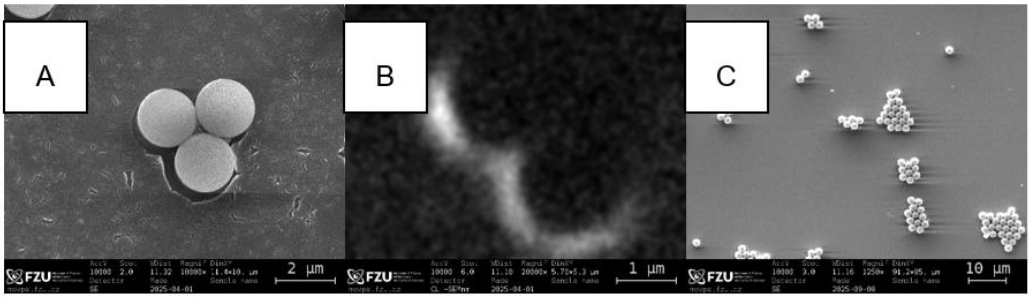

Figure 5 Metal deposition; 50 nm Cr layer with visible cracks (A), CL measurement, GaN - white area, Cr - black area (B), Ti/Cr after SDS cleaning, layer is defect free (C)

3.4 Sphere lift-off

Sphere lift-off is a crucial part of whole fabrication process. An efficient method to remove the PS spheres from the sample surface is to submerge it in the ethanol and apply mild sonification for 30 seconds (**Figures 6A, 6B**). To remove all spheres this process was repeated multiple times. Samples, where SDS had not been removed were damaged even by mild sonification, which manifested by flaking of metallic layer after few seconds. To assess the damage, the EDX investigation was performed (**Figure 6D**). The Flaking was eliminated by refining metallic deposition mentioned in chapter 3.3. Alternatively, it is possible to dissolve polystyrene in cyclohexanone after 1 minute (**Figure 6C**). Dissolving the PS spheres leaves behind the leftover metallic caps, that previously covered each sphere. The cap is easily removed in ultrasonic bath with only few pulses, thus limiting damage to the protected area.

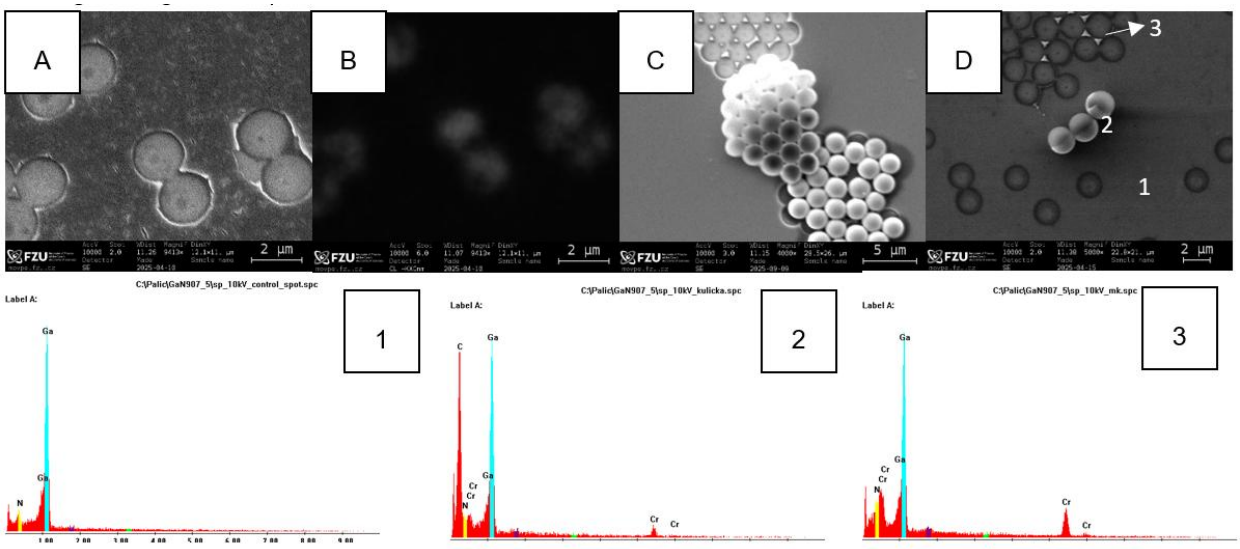

Figure 6 Lift-off; Lift-off in ethanol and ultrasound bath (A), CL measurement of the same place, GaN (white), Cr (black) (B), dissolved spheres in cyclohexanone, Cr residual can be removed in ultrasound bath (few pulses) (C), EDX investigation after ethanol and ultrasound lift-off (D), Complete destruction of the Cr layer in ultrasound bath, only GaN in the spectrum (1). Partial survival of Cr mask (2), Cr covered residual spheres after lift-off (3)

3.5 Plasma etching

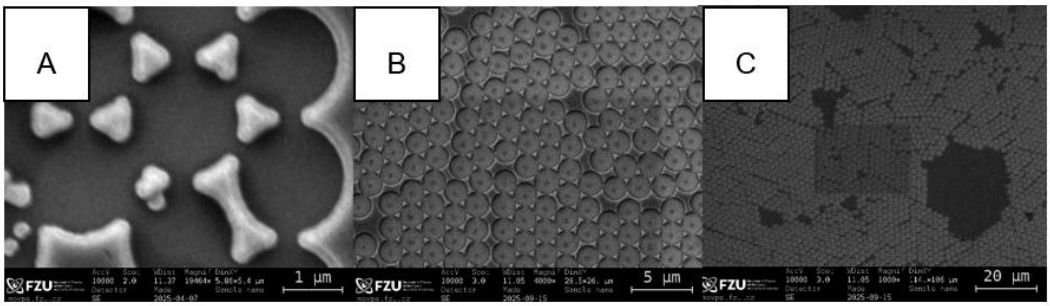

Figure 7 Trigonal structures; etching time = 10 min (A), Large array up to 1 cm^2 (B, C)

$SiCl_4$/Ar plasma etching was performed to finalize the nanostructure fabrication. Using the selected parameters, the etching rate was about 60 nm/min for GaN on the exposed areas. Cr or Ti/Cr successfully protected the triangular areas between the spheres. The thickness of the Cr layer should be sufficient so that

it survives whole etching duration. Cr layer 100 nm thick should withstand etching for 5 minutes. As a result of the plasma etching, an array of triangular nanostructures was fabricated. The size of the individual nanostructure was about 500 nm (**Figure 7A**). Due to the imperfect monolayer coverage other shapes were also observed (**Figures 7B, 7C**). Similar structures have been reported in article [6].

4. CONCLUSION

It has been demonstrated that nanosphere lithography is suitable method for fabricating nanostructures with large surface area. Of the three methods used, the water interface method proved to be the best approach due to its reliable formation of a monolayer, which is essential for the whole process. The entire fabrication process still requires further refinement, although improvements have been achieved such as the addition of SDS to improve monolayer self-assembly. Successful Ti/Cr deposition was also demonstrated after thorough predeposition cleaning to remove residual SDS, which was causing weak adhesion between the sample and the metallic layer. The lift-off process was also improved, where it was empirically discovered that the mild sonification is enough to remove the spheres from the sample. If even the mild sonification damages Ti/Cr protected area, it is also possible to dissolve the PS spheres in cyclohexanone. $SiCl_4$/Ar plasma was successfully utilized to etch GaN samples with etching rate of 60 nm/min. The desired trigonal nanostructures had dimensions of around 500 nm, although other shapes were also observed due to imperfections in the sphere monolayer. It was demonstrated that NSL can be used reliably with samples up to 1 cm².

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