Effect of wet KOH etching on structural properties of GaN nanowires grown on patterned SiO$_x$/Si substrates

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Abstract. The possibility of the controlled removal of GaN nanowires (NWs) from an SiO$_x$ inhibitor layer of patterned SiO$_x$/Si substrates has been demonstrated. It has been found that the wet KOH etching preserves the selectively grown GaN NWs on Si surface, whereas the GaN NWs grown on inhibitor SiO$_x$ layer are removing. The effect is described by the difference in polarity between GaN NWs grown on a Si surface and NWs grown on a SiO$_x$ inhibitor layer.

1. Introduction
Nanowires based on III-N materials are the promising structures for creation of nanoscale light emitting diodes (LEDs), sensors, transistors, solar cells and water-splitting cells [1]. Moreover, NWs based devices can surpass their semiconductor layers-based counterparts due to a larger surface area and sufficiently lower structural defects associated with lattices mismatch between the growing structure and the substrate. A particular attention is focusing on Ga-polar GaN NWs, since the devices based on them demonstrated an excellent high-power and high-frequency performances [2, 3]. At the same time, selective-area growth (SAG) of NWs by molecular beam epitaxy (MBE) has shown high potential for synthesis defect-free NW arrays for opto- and nanoelcotronics, and piezotronics [4]. This approach allows to synthesize nanowires with defined density, location and size and is based on the growth of nanostructures in the preliminary formed pattern which is generally consists of inhibitor layer (for example, SiO$_x$) and the ordered holes in it. However, there is the undesirable growth of nanowires on the inhibitor layers is often observed, which creates problems for the subsequent application of the structures. A possible solution to this problem would be the application of a non-defect selective etching process that would remove undesirable nanowires.

In the work, we investigate the influence of the wet chemical etching in potassium hydroxide (KOH) aqueous solution, as a possible approach of the non-defect selective etching, on the GaN NWs grown both on SiO$_x$ inhibitor layer and in the holes of the patterned SiO$_x$/Si substrates.

2. Experimental
Arrays of GaN NWs on patterned SiO$_x$/Si(111) substrates which had been prepared using photolithography through a close-packed array of microspherical lenses [5] were synthesized by MBE at Riber Compact 12 MBE system. As previously reported in [6], at the growth temperature of about
815 °C, GaN NWs were formed both in the holes on the surface of Si and on the SiO_x inhibitor layer. Structural properties of the samples were studied with Zeiss Supra 25 scanning electron microscopy (SEM). The grown GaN NWs on Si had an average height of about 2.2 μm and a diameter of 370 nm, while the NWs grown on SiO_x layer had a height of 1.75 μm and a diameter of about 70 nm (see Figure 1).

![Figure 1. Typical SEM images of initially GaN nanowires in top view (a) and in isometric view geometry (b).](image)

3. Results and discussion
The selective etching of GaN NWs was carried out using a potassium hydroxide (KOH) aqueous solution (1:5) at a temperature of 75 °C with duration from 1 to 7 minutes. The etching of GaN NWs is described via the following reactions [7]:

\[
2GaN + 3H_2O \xrightarrow{KOH} Ga_2O_3 + 2NH_3 \tag{1}
\]

\[
GaN + 3H_2O \xrightarrow{KOH} Ga(OH)_3 + NH_3 \tag{2}
\]

In the reactions above KOH acted as a catalyst for the formation of gallium oxide (1) and gallium hydroxide (2). At the same time, it acted as a solvent for these compounds which provides the etching process.

3.1. Impact of etching time
It has been found that etching with every step reduces the density of GaN nanowires on SiO_x layer, as shown in Figure 2. With an increase in the etching time, the GaN NWs on the inhibitor layer degraded to complete removal. At the same time, the dimensions and morphology of NWs grown in the holes did not change significantly within the equipment error. So, it means that the etching rate of NWs grown on the SiO_x layer was significantly higher than that of NWs grown in the holes on Si surface.
3.2. Identification of NWs polarity

It was observed that the etching process specifically changes morphology of GaN NWs grown on the inhibitor SiOₓ layer. An interaction of the etching solution with the NWs led to the formation of hexagonal pyramid-like tops of GaN NWs grown on the inhibitor layer, as can be seen in figure 3b (figure 3a below shows a SEM image of the initial GaN NWs to give a clear comparison). In combination with different etching rates of the NWs, such etching mechanism corresponds to the N-polar GaN NWs [8-11]. So, the difference in the crystallographic polarity of nanowires on the inhibitor layer and in the holes successfully explains the difference in etching rates. The susceptible to etching GaN NWs on the inhibitor layer are identified as N-polar and, in contrast, the resistant to wet KOH etching NWs on the surface of Si are identified as Ga-polar.

4. Conclusion

In summary, the processing in a KOH solution makes it possible to produce consistent ordered arrays of Ga-polar GaN NWs synthesized by the selective-area MBE method on patterned SiOₓ/Si(111) substrates. It was demonstrated that wet KOH etching allows maintaining the morphology of NWs grown on Si surface, meanwhile, degrading the NWs on the inhibitor layer. We have determined that the GaN NWs grown in the holes have a Ga-polarity, while the ones on SiOₓ surface have an N-polarity.

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Conflict of interest

The authors declare that they have no conflict of interests.
References

[1] Blumberg C, Häuser P, Wefers F, Jansen D, Tegude F-J, Weimann N and Prost W 2020 *CrystEngComm* **22** 5522-5532

[2] Palacios T, Chakraborty A, Heikman S, Keller S, Denbaars S P and Mishra U 2006 *IEEE Electron Device Lett.* **27** 13

[3] Wu Y F, Saxler A, Moore A, Smith R P, Sheppard S, Chavarkar P M, Wisleder T, Mishra U K and Parikh P 2004 *IEEE Electron Device Lett.* **25** 117

[4] Roshko A, Brubaker M, Blanchard P, Harvey T and Bertness K 2018 *Crystals* **8**(9) 366

[5] Dvoretckaya L N, Mozharov A M, Fedorov V V, Bolshakov A D and Mukhin I S 2018 *J. Phys.: Conf. Ser.* **1124** 022042

[6] Gridchin V O, Kotlyar K P, Reznik R R, Dvoretskaya L N, Parfen’eva A V, Mukhin I S and Cirlin G E 2020 *Tech. Phys. Lett.* **46**(11) 1080-1083

[7] Guo W, Kirste R, Bryan I, Bryan Z, Hussey L, Reddy P, Tweedie J, Collazo R and Sitar Z 2015 *Appl. Phys. Lett.* **106** 082110

[8] Guo W, Xie J, Akouala C, Mita S, Rice A, Tweedie J, Bryan I, Collazo R and Sitar Z 2013 *J. Cryst. Growth* **366** 20

[9] Hestroffer K, Leclere C, Bougerol C, Renevier H and Daudin B 2011 *Phys. Rev. B* **84**(24)

[10] Eftychis S, Kruse J, Koukoula T, Kehagias T, Komninou P, Adikimenakis A and Georgakilas A 2016 *J. Cryst. Growth* **442** 8-13

[11] Wu C H, Lee P Y, Chen K Y, Tseng Y T, Wang Y L and Cheng K Y 2016 *J. Cryst. Growth* **454** 71–81