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Nanometer scale patterning of GaN using nanoimprint lithography and Inductively Coupled Plasma etching

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ABSTRACT

In this paper results on GaN patterning using nanoimprint technology are presented. Direct method of stamp fabrication based on FIB etching was used. Stamp with critical dimensions of 50 nm was achieved. Two kinds of polymer materials were used for master stamp replication. Influence of etching parameters using chlorine based plasma on GaN etch rate and surface roughness was discussed. Triple mask consisting of TU2 resist, Cr and SiO_2 used for NIL-generated pattern transfer into GaN allowed successful patterning.

1. Introduction

GaN and related materials due to their properties such as wide band gap, high thermal conductivity, high breakdown voltage and chemical stability are materials of choice for fabrication of UV, blue and white light-emitting diodes LED and lasers [1,2], high temperature devices and high frequency high power devices [3,4]. Structures as small as few tens of nanometers have been intensively studied due to their ability to enhance device operation efficiency. Apart from the most frequently used e-beam lithography [5–7], nanoimprint lithography (NIL) has been successfully used as a fast and low-cost alternative method for nanometer scale structure fabrication to produce periodic structures such as: photonic crystals [8,9], gratings [10,11], or transistor gates [12,13]. In the case of GaN the fabricated pattern may only be used as a mask for pattern transfer, irrespectively of the patterning technique. Due to high resistance of GaN to most chemicals the most suitable pattern transfer process is plasma etching applying the Inductively Coupled Plasma (ICP) technique in chlorine-based gasses such as BCl_3 and Cl_2 [14,15].

The purpose of presented work was to develop process for nanometer patterns fabrication in GaN using NIL and ICP techniques. The work concerns master and soft stamps fabrication processes. Prior to patterning using above techniques, optimization of GaN etching parameters was carried out. Finally, triple mask for imprinted patterns transfer was proposed.

2. Experimental

The GaN samples used in the experiment were: (a) n-type and p-type doped with carrier concentration of about $2 \cdot 10^{18}\ cm^{-3}$ and $2 \cdot 10^{19}\ cm^{-3}$ grown by metalorganic vapour phase epitaxy (MOVPE) on sapphire (0001) substrates, provided by TopGaN, (b) p-type doped with carrier concentration of about $3 \cdot 10^{17}\ cm^{-3}$ grown by molecular beam epitaxy (MBE) on silicon (1 1 1) substrate, provided by IFPAN, (c) n-type and p-type doped bulk material with carrier concentration of about $5 \cdot 10^{16}\ cm^{-3}$ and $1 \cdot 10^{18}\ cm^{-3}$ grown by ammonothermal method, provided by Ammono. The thickness of GaN was about 8 μm, 1.5 μm, 1 μm and 300 μm for n-type MOVPE-grown, p-type MOVPE-grown, MBE-grown and bulk, respectively. Schematics of master stamp as well as soft stamp fabrication are shown in Fig. 1 and Fig. 2. BGL-GZ83 agent provided by Profactor was used as an anti-sticking layer. An IPS® polymer foil provided by Obducat and inorganic–organic hybrid polymer ORMOCER® OrmoStamp provided by Microresist were used as the soft stamp material. TU2 resist was used for imprinting processes. The criterion of imprinted pattern quality evaluation was the residual resist layer thickness, accepted up to 8 nm as well as the agreement of polymer stamp pattern dimension with the imprinted pattern size to be with ±10% tolerance. GaN samples have been etched using ICP BCl_3/Cl_2 plasma in the Oxford Instruments System

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100 ICP 180. As a mask for testing etch processes the resist S1818 was used. Influence of gas composition in the ranges 5–40/5–30 sccm, RF power of 5–50 W, ICP power of 600–1100 W, pressure of 5–25 mTorr and temperature of 20–80 °C on GaN etch rate and surface morphology were investigated. Scheme of NIL-generated patterns transfer into GaN is shown in Fig. 3. Measurements of dimensions of master and soft stamp patterns, dimensions of imprinted patterns, etched surface morphology as well as patterns depth were determined by Innova Atomic Force Microscope and Helios NanoLab Dual Beam FIB Microscope. 10 nm of Au was deposited on the polymer stamps to enable SEM examination.

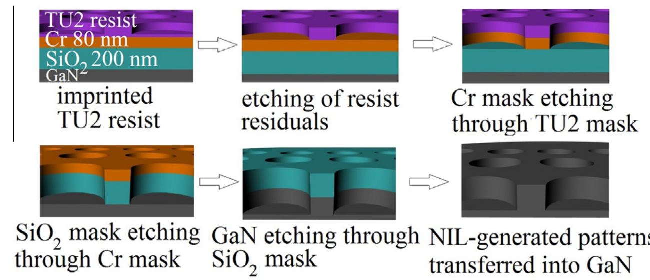

Fig. 3. Schematic diagram of GaN patterning.

3. Results and discussion

3.1. Master stamp fabrication using FIB

Initial material for master stamp was a 2 × 2 cm^2 glass plate covered with 100 nm thick chromium layer. The fabrication of the master stamp pattern consisted in removing the whole Cr layer by Ga^+ ions direct etching in specific places according to designed shape. The design for FIB etching was prepared as black and white bitmap files (with white pixels to be etched) in the form of rectangles, squares and circles. Critical dimensions of prepared designs were both 50 nm and 100 nm (side of rectangle or square, circle diameter). The applied ion energy was 30 keV and several ion beam currents in the range of 9.7–1.5 pA were checked. Based on obtained results for further process optimization the current of 1.5 pA has been chosen. For the selected beam current an optimization of the etching process consisted of the determination of the most accurate values of two parameters: (i) the dwell time, tested in the range of 0.2–0.8 ms (i.e. the period during beam scanning of the pattern when one pixel is etched during a single scan) and (ii) the number of scans, tested in the range of 3–24. We found that for the described Cr layer the optimal dwell time was 0.4 ms and the number of scans necessary to etch the Cr layer down to the glass substrate was equal to 8. For higher and lower dwell times the obtained pattern was deformed or blurred. The reason is that when the pattern is scanned with high speed (i.e. with low dwell time) then the beam blanker needs to switch on/off the beam with a high frequency and its limited time response may cause blurring of the etched pattern. On the contrary, when the dwell time is too long, then the beam stays too long at one point and the secondary re-deposition of previously etched material occurs, i.e. the etched pattern becomes deformed. Examples of master stamp produced using optimized parameters are shown in Fig. 4.

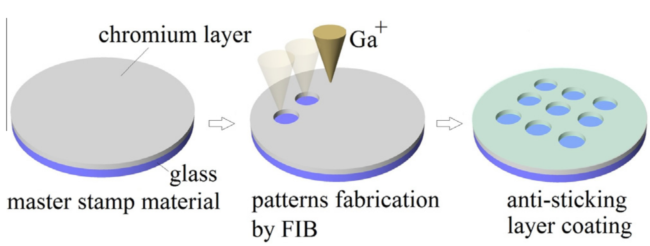

Fig. 1. Schematic diagram of master stamp fabrication.

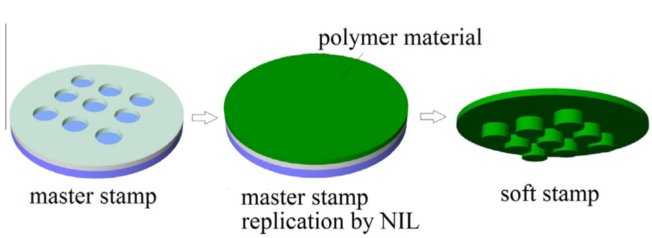

Fig. 2. Schematic diagram of soft stamp fabrication.

3.2. Soft stamp fabrication

The soft stamps were made by a polymer molding method using thermal and UV NIL modes, for IPS foil and OrmoStamp, respectively. In the case of polymer foil, firstly the melting temperature was found experimentally. For that purpose seven temperatures were checked starting with 100 °C up to 160 °C with a 10 °C step. Pressure and time were constant and equal 60 bar and 60 s, respectively. For these conditions the melting temperature was established at 150 °C. Next, in a similar way appropriate pressure and time were found. Agreement of produced polymer patterns dimensions with master stamp patterns as well as the height of obtained pattern was a criterion of parameters selection. The best results have been achieved for the following parameters: $p = 40$ bar, $T = 150$ °C, $t = 60$ s. Owing to the character of OrmoStamp material the most influencing parameter was found to be the dose of UV irradiation causing solidification of initially fluent polymer material. The applied dose was controlled by the time of irradiation in the range of 30 s up to 300 s. The shortest time providing complete solidification of OrmoStamp was found to be 120 s. Examples of soft stamps fabricated applying experimentally selected conditions are shown in Fig. 5 and Fig. 6. Achieved agreement of soft stamp features dimensions with the master stamp features was in the ranges of ±3% up to 18% and ±6% up to 10% for critical dimensions of 50 nm and 100 nm, respectively.

3.3. GaN patterning

Chemical mechanism of GaN etching in BCl_3/Cl_2 plasma consists of a reaction of Cl^- and BCl^{2+} ions with GaN substrate to form volatile $GaCl_x$ byproducts. The influence of gas flow ratio of Cl_2 to BCl_3 on etch rate of GaN was shown in Fig. 7. It is known that Cl_2 dissociates more readily than BCl_3 in this plasma. That is why an increase of Cl_2 mole fraction (shown in Fig. 7) causes increasing yield of Cl atoms resulting in an increase of the etch rate [16]. On the other hand, addition of BCl_3 decreases the etch rate but considerably increases the GaN etch selectivity over the mask. It is caused by wetting properties of BCl_3 which reduce surface oxidation. Influence of etching parameters on the etched pattern depth was shown in Fig. 8 and Fig. 9. Analysis of obtained results pointed out a constant dependence. The deepest and the shallowest cavities were observed for p-type MOVPE epi-GaN and p-type bulk GaN respectively. As was shown in Fig. 8a, the etch depth increases with an increase in RF power. This is caused by the increase of electron energy causing an increase of ionization. Additionally, high negative filed is built close to the cathode causing acceleration of ions towards electrode.