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APPLICATION OF SURFACE CHARGE LITHOGRAPHY TO NANOSTRUCTURING OF GaN EPILAYERS

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Introduction

Recently we demonstrated that low-energy Ar^+ ion beam treatment of n-GaN epilayers with subsequent photoelectrochemical etching (PEC) in aqueous solution of KOH can be used for material microstructuring [1]. The low-energy ion beam treatment creates surface defects which trap electrons thus generating a surface layer of negative charge. The ion-beam-induced surface layer of trapped negative charge shields GaN against PEC etching. The new approach was called Surface Charge Lithography (SCL) taking into account the possibility to design and exploit the surface charge trapped by ion-beam-induced radiation defects as lithographic mask for the purpose of manufacturing GaN mesa-structures [1]. We found that the mesa-structures fabricated by using ion beam treatment with subsequent PEC etching of n-GaN epilayers exhibit an undercut of about 200 nm determined by the hole diffusion length [1]. The reason is that due to lateral diffusion of minority carriers partial etching occurs under the mask which is the top area damaged by the ion beam. The undercut etching made it questionable the ability to fabricate GaN mesa-structures with transverse dimensions less then the hole diffusion length. In this work, we demonstrate the possibility to fabricate GaN nanowalls with transverse dimensions as low as 100 nm using direct “writing” of protective masks by a focused ion beam (FIB) with subsequent subjection of samples to photoelectrochemical etching in aqueous solution of KOH.

Experiment

The GaN layers used in our experiments were grown by low-pressure metalorganic chemical-vapor deposition (MOCVD) on (0001) c-sapphire. A buffer layer of about 25-nm-thick GaN was first grown at 510 °C. Subsequently a 0.5-μm-thick n-GaN followed by a Si-doped n^+-GaN film and a top n-GaN layer with 2.0 μm thickness each were grown at 1100 °C. The concentration of free electrons in the top n-GaN layer was 1.7×10^{17} cm^{-3}, while the density of threading dislocations was in the range of $10^9 – 10^{10}$ cm^{-2}.

An FEI Strata FIB 201 focused ion beam system was used for exposure of the gallium nitride samples. This instrument produces a focused gallium ion beam of 30 keV energy with beam currents in the range 1 pA to 12 nA, and corresponding beam diameters of 8 nm to 500 nm. For the exposure of the gallium nitride here, a beam current of 150 pA was used. The exposure pattern was created in bitmap form, with 1024 x 1024 pixel format, covering an area of 122 μm square on the sample. An exposure time of 1 μs per pixel gave a total exposure time for the pattern of 0.48 s, and a corresponding exposure dose of 6.6×10^{12} cm^{-2}. Stopping range calculations predict main projection range of Ga ions in the GaN layer of about 14 nm at these conditions.

PEC etching was carried out in stirred 0.1 mol aqueous solution of KOH under in situ UV illumination provided by focusing the radiation of a 350 W Hg lamp to a spot of about 5 mm in diameter on the GaN surface exposed to electrolyte. No bias was applied to the sample during etching. The morphology of etched samples was studied using a TESCAN scanning electron microscope (SEM) operating at 20 keV.

Micro-Raman measurements were performed using a Renishaw InVia spectrometer and a 488 nm laser line of an Ar+ ion laser. The laser beam was focused on the sample surface using 50x microscope lens into a spot of 0.5-0.7 μm diameter. The micro-Raman spectra were recorded at room temperature using backscattering geometry.

Before PEC etching, selected GaN surface areas with dimensions of 100 x 0.1; 100 x 0.2; 100 x 0.5; 100 x 1; 100 x 2; 100 x 5; 100 x 10 and 100 x 50 μm^2 were uniformly treated by the focused ion beam. Fig. 1 illustrates the SEM image taken from a surface region subjected to FIB treatment followed by PEC etching for 30 min.

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It is evident that only areas not subjected to ion beam treatment are vulnerable to photoelectrochemical attack. In the etched areas whiskers representing remaining GaN material containing threading dislocations [1-3] can be easily distinguished. At the same time the FIB treated areas prove to be resistant to PEC attack in spite of the fact that these areas exhibit some micrometer-size defects related to the growth process. The feather-like extension (marked by white arrow) of the rectangle with dimensions of 100 x 50 μm^2 is likely to be associated with a mechanical scratch on the surface which can make GaN resistant to PEC etching as well [1].

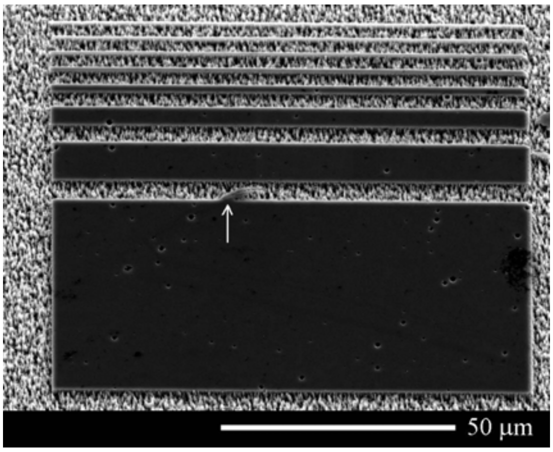

Fig. 1. SEM image taken from n-GaN sample subjected to FIB treatment followed by PEC etching for 30 min. Dimensions of mesastructures (from top to bottom), μm^2*: 100 x 0.1; 100 x 0.2; 100 x 0.5; 100 x 1; 100 x 2; 100 x 5; 100 x 10 and 100 x 50. Marked by white arrow is a feather-like extension, see text for details*

The advantage of low-energy focused ion beam writing combined with PEC etching is that it allows easily to create nanostructures, which are practically limited by the resolution of the ion beam system. It is rather spectacular that this maskless approach leads to the formation of thin walls with the thickness as small as 100 nm. The 100-nm thick walls are bright in SEM images due to charging phenomenon. Observation of charging phenomenon is indicative of the wall low conductivity which may be caused by depletion of free carriers. It is known that the Fermi level at the surface of n-GaN is pinned at 0.5-0.7 eV below the bottom of the conduction band [4,5] and this phenomenon leads to the formation of the depletion space charge layer of about 70 nm for n-type doping level in our samples. Taking this into account, one may assume that the surface depletion layers related to two lateral sides of the 100-nm thick wall merge resulting therefore in poor wall conductivity.

The SEM image in Fig. 2 illustrates a region subjected to FIB treatment followed by PEC etching for 60 min. The analysis shows that the height of GaN walls in this image is higher than the height of walls formed after etching for 30 min (Fig. 1). Note the reduced density of whiskers in areas between the GaN walls in Fig. 2 in comparison with that inherent to such areas in Fig. 1. Most remarkably, that no undercut etching is observed in case of very thin GaN structures fabricated by surface charge lithography.

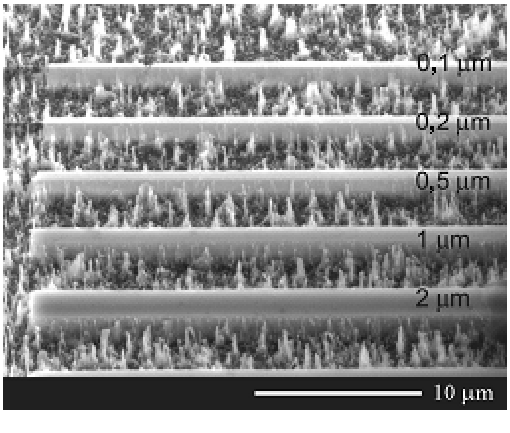

Fig. 2. SEM image taken from n-GaN sample subjected to FIB treatment followed by PEC etching for 60 min. Dimensions of mesostructures (from top to bottom), μm^2*:100 x 0.1; 100 x 0.2; 100 x 0.5; 100 x 1; 100 x 2*

As one can see from Fig. 2, the morphology of the 2-μm width mesastructure reflects the impact of undercut etching (charging effect allows one to visualize the undercut in SEM images as bright periphery areas of the mesostructures [1]), while the 100-nm wide nanowall exhibits no traces of the undercut. One may conclude that in structures below a critical width defined by FIB-induced surface charge mask no undercut etching occurs. Such critical width seems to be defined as twice the extension of the surface depletion layer width. Note that for n-GaN with free electron concentration of the order of 10^{17} cm^{-3} the depletion space charge layer is of about 70 nm. Under such conditions the 100-nm thick walls are fully depleted of free carriers and therefore cannot support current flow. Taking into account that current flow is essential for PEC etching process, it is clear that the undercut etching will not take place in spite of the fact that the minority carrier diffusion length can reach values as high as 200 nm [1].

To estimate the degree of crystal lattice disorder induced by FIB processing, we studied micro-Raman scattering spectra of n-GaN samples subjected to FIB treatment at doses 6.6 x 10^{11}; 6.6 x 10^{12}; 8.0 x 10^{13} and 7.7 x 10^{14} cm^{-2}. Raman spectra in Fig. 3 show two allowed Raman modes of 0001-oriented GaN material, namely E_2 and A_1LO at 569 and 735 cm^{-1}, respectively. Since GaN is transparent to the 488 nm excitation, modes of sapphire substrate are visible at 418 and 750 cm^{-1}.

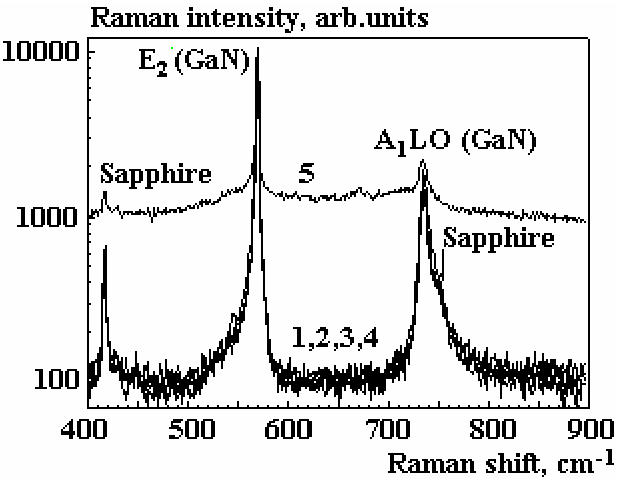

Fig. 3. Raman scattering spectra of n-GaN samples subjected to FIB treatment at doses, cm^{-2}: 1 – as-grown, 2 −6.6 x 10^{11}; 3 − 6.6 x 10^{12}; 4 −8.0 x 10^{13}; 5 − 7.7 x 10^{14}

The spectra of samples irradiated with ions at doses up to 8.0 x 10^{12} cm^{-2} are practically identical to that of as-grown n-GaN specimen. Taking into account that the frequency and width of the phonon bands in Raman spectra of semiconductor compounds are dependent upon the amount of the crystal lattice damage [6], one may conclude that the ion beam treatment at doses up to 8.0 x 10^{13} cm^{-2} generates lattice point defects at relatively low densities limited to the surface region of the GaN layer, about 15 nm in our case. The crystalline quality of the material as a whole is negligibly disturbed. According to the data presented in Fig. 3, only the highest dose of irradiation, i.e. 7.7 x 10^{14} cm^{-2}, leads to pronounced changes in the Raman spectrum. The visible 488 nm excitation normally penetrates whole thickness of the 2.5 μm thick GaN layer, however implantation of Ga ions at the doses above 10^{13} cm^{-2} reduces optical penetration depth of laser beam and Raman signal becomes more sensitive to the ion bombardment damage on the surface. Note the reduced intensity ratio between GaN and sapphire substrate peaks.

Thus, surface charge lithography proves to be an efficient tool for both micro- and nanostructuring of gallium nitride. Moreover, in case of fabrication of nanostructures with transverse dimensions equal to or less than the double surface depletion layer no undercut etching related to the minority carrier diffusion occurs. We believe that further improvement of GaN growth technology will allow one to fabricate high quality nanostructures by maskless FIB direct writing with subsequent PEC etching.

This work was supported by the Supreme Council for Research and Technological Development of Moldova.

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Received 03.12.07

Summary

It is shown that treatment of GaN epilayers by a low energy low dose focused ion beam with subsequent photoelectrochemical etching represent an efficient tool for GaN nanostructuring. Direct “writing” of surface negative charge trapped by radiation defects allows one to fabricate thin GaN walls with the thickness as low as 100 nm using focused ion beam treatment. The obtained results show that the undercut etching inherent to GaN etching through windows defined by surface charge lithography depends on the depletion length in doped GaN material and does not occur in the structures below critical size of 200 nm in our case.