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Fabrication of Micro- and Nano-craters on the Surface of GaN Substrates by Using Wet-chemicals Assisted Femtosecond Laser Ablation

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We have investigated micro and nano fabrication of wide-bandgap semiconductor Gallium nitride (GaN) using a femtosecond (fs) laser. Nanometer scale crater is successfully formed by wet-chemicals assisted fs laser ablation, in which the laser beam is focused on single-crystal GaN substrates in a hydrochloric acid solution. This method can efficiently remove the ablation debris due to chemical reactions, resulting in high quality ablation. On the other hand, a two-step processing method, i.e., irradiation with fs laser in air followed by wet etching, distorts the shape of crater because of the residual debris. Threshold fluence for wet-chemicals assisted fs laser ablation is lower than that for fs laser ablation in air. This effect is advantageous to the improvement of fabrication resolution. At present, we have achieved the fabrication of crater as small as 510 nm by using a high NA (0.73) objective lens.

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1. Introduction

Gallium nitride (GaN) has attracted attention over recent years because it is a wide band gap semiconductor applicable to a variety of optical devices, such as light emitting diode (LED), laser diode (LD) and so on. Therefore, development of microfabrication techniques for GaN is quite important. Generally, plasma etching [1-3] or reactive-ion etching processes [4-6] are utilized for fabrication of semiconductors. In the case of GaN, however, high chemical stability and high hardness interfere with high speed and high quality etching. On the other hand, laser ablation processing is promising for improvement of fabrication efficiency [7-9]. So far, our group has reported that multiwavelength laser ablation techniques were applicable to the microfabrication of GaN [10-12]. Although these methods permit the high–quality ablation with little thermal damage, they have a problem. Namely, the reaction is limited to the surface of material, which means only two dimensional structure can be fabricated. In these days, more complicated and 3D devices are desired, so we chose a femtosecond (fs) laser ablation process.

As is well known, the intensity of focused fs laser is so high that multiphoton absorption takes place at the localized area near focal point. Ablation reaction as well as many kinds of processes including electron excitation, ionization, and phase transition is induced by irradiation with fs laser. In this work, we have investigated the possibility of nanometer scale fabrication of GaN single crystal by using fs laser. In multiphoton absorption, the effective spot size can be reduced, and then micro- or nano-fabrication will be realized.

2. Experimental

The material used in this work was commercially available single-crystal gallium nitride (GaN) substrate from Kyma Technologies Incorporated, which shows n-type conduction. The substrate has [0001] out-of-plane orientation, and the thickness is 470 μm. We utilized a fs laser system (Clark-MXR, CPA-2001) emitting a pulse width of 150 fs [full width at half maximum (FWHM)], a wavelength of 775 nm and a repetition rate of 1 kHz. The laser beam, the diameter of which was reduced to 3 mm by an aperture, was focused to the surface of material by a 20x microscope objective with a numerical aperture (NA) of 0.46. The GaN substrates under fabrication were translated using a PC controlled x-y-z stage with a resolution of 0.5 μm. The surface of GaN is irradiated with fs laser in air, and then, a successive etching process in a 35% hydrochloric (HCl) acid solution is performed for an hour (hereinafter referred to as two-step processing method). We have also carried out wet-chemicals assisted ablation processing, in which the laser beam is directly focused on the substrates in an HCl solution. The morphology and size of the ablation craters formed by a single fs-laser pulse are investigated by using atomic force microscope (AFM) and optical microscopy. The change of chemical composition in ablated area is examined using X-ray photoelectron spectroscopy (XPS) measurement.

3. Results and discussion

Surface and cross-sectional morphologies of typical ablated craters formed on the surface of GaN by using two-step processing method are shown in Fig. 1. The pulse energy of fs laser was 80 nJ. In the first step, namely single-pulse irradiation with a fs laser, ablation reaction takes place. The ablated surface is strongly roughened and the edge of crater is unclear due to residual debris as shown in the AFM image (upper side) of Fig. 1(a). After etching process in HCl solution, the debris is removed to some

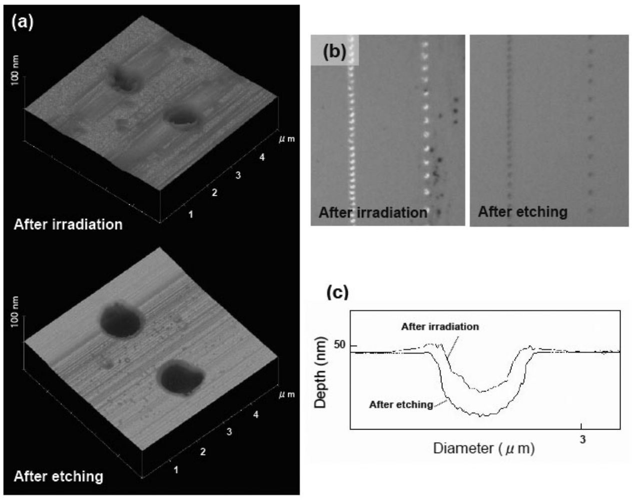

Fig. 1 Surface and cross-sectional morphologies of typical ablated craters formed on the surface of GaN by using two-step processing method.

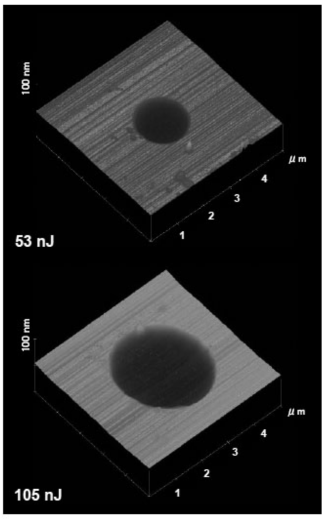

Fig. 2 Morphology of ablation crater formed by wet-chemicals assisted fs laser ablation

degree, and as a result, the edge becomes somewhat clear (lower side). However, the crater's shape is a little distorted and the roughness does not disappear entirely. Figure 1 (b) presents the optical micrographs before and after etching, respectively. The irradiated area is bright spot due to high reflectivity before etching process. It is anticipated that a Ga-rich phase with metallic reflectivity is formed on the ablated surface [7]. On the other hand, the ablation craters become dark after etching. According to the cross-sectional survey provided in the Fig. 1 (c), the depth of ablation crater increases from 26 to 40 nm and the diameter also increases from 0.92 to 1.3 μm in this irradiation condition. We speculate that most part of the layer etched in HCl solution is the Ga-rich phase. The etched surface is so rough that light scattering occurs, resulting in the decrease in reflectivity. In order to support this speculation, the chemical compositions are examined using XPS measurement. The ratios of Ga to N for each step are summarized in Table 1. In the surface of GaN which is not irradiated with fs laser, the ratio is higher than 1, because the edge of surface is Ga face. After irradiation, the ratio increases to 1.82. Then, the value decreases to 1.67 after etching in HCl solution for 1h. This change of chemical composition is explainable in terms of the formation and the removal of a Ga-rich layer.

Table 1 Ratios of Ga to N obtained byXPS measurement

	Unirradiated	Irradiated	Etched in HCl
Ga / N	1.56	1.82	1.67

Thus, two different reactions concurrently occur in the two-step processing method. Near the center of focal point, in which the laser intensity exceeds the ablation threshold, direct ablation takes place. In the meanwhile, at the surrounding area where the laser intensity is below ablation threshold, thermal reaction is dominant due to relaxation of excited electrons, and then a Ga rich layer is formed. By the successive etching process, HCl solution dissolves the metallic layer, resulting in wider craters.

Figure 2 shows the AFM images of ablation craters formed by irradiation in HCl solution, namely wet-chemicals assisted fs laser ablation. The pulse energies of fs laser are 53 and 105 nJ respectively. Symmetrical-round-shaped craters are formed with much higher quality compared with two-step processing. The quality became lower with the decrease in the concentration. Obviously, the HCl solution plays an important role in the high quality fabrication. One can suppose that the laser interaction with GaN should be similar to the case of two-step processing. However, the features of fabricated structures are somewhat different. For example, Figure 3 shows the cross-sectional profiles. As the pulse energy is increasing, the difference of shape becomes more significant between two methods. Figure 4 presents the pulse energy dependence of etching depth. We can observe the two characteristic dif-

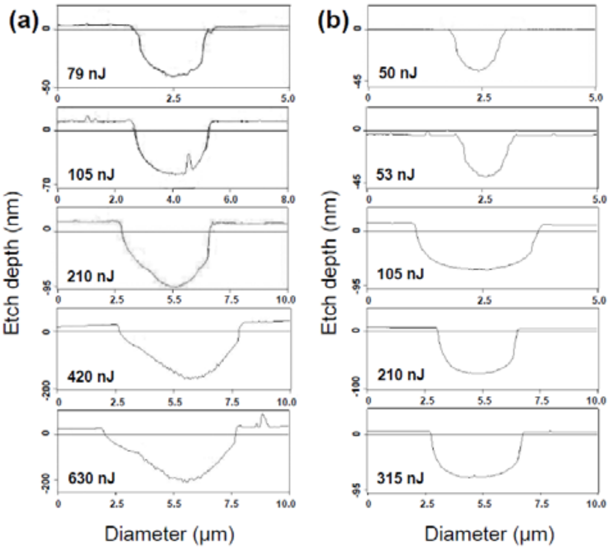

Fig. 3 Cross-sectional profiles of ablation craters formed by (a) two-step processing method and (b) wet-chemicals assisted fs laser ablation.

ferences. First, the threshold energy for the case of wet-chemicals assisted ablation is lower than that of two step processing. We also observed that the threshold shifted to higher energy as the concentration became lower. It is inferred that photochemical reaction by HCl is responsible for the high quality ablation. Second, the etch depth for single pulse is saturated around 80 nm in the case of wet-chemicals assisted ablation. As a result, the craters' bottoms become flat (see Fig. 3). Although the detailed mechanism of this processing method is still not clear, it is obvious that the HCl solution has an important role in greatly improving the etching quality.

An improvement of fabrication resolution is also of great interest because of the potential application for a variety of highly integrated microdevices. In the case of two-step processing, 1.3-μm-diameter crater is formed by single pulse at energy of 80 nJ. On the other hand, the minimum ablation crater, the diameter of which is as small as 1.1 μm, can be produced at pulse energy of 47 nJ by using the wet-chemicals assisted fs laser ablation technique. The results suggest that the wet-chemicals assisted ablation is promising method for higher resolution. High NA (0.73) and long working distance (4.7 mm) objective lens (100x) was utilized for the nano-fabrication. By using this objective lens, the spot size at around focal point decreases to 1.75 μm, while the spot size using 20x objective is 2.78 μm. Figure 5 shows AFM image of fabricated nano-scale crater, the diameter of which is as small as 510 nm using wet-chemicals assisted fs laser ablation. It is speculated that the higher resolution of this method compared to the two-step processing method is ascribed to the cooling effect of liquid solution. The Ga-rich layer is formed at around the region where the beam intensity is below the ablation threshold. The heat conductivity of liquid solution is higher than that of air. Therefore, in the case of the wet-chemicals assisted ablation, part of the excess heat generated during and after ablation reaction diffuses into HCl solution. As a result, formation of a Ga-rich layer is suppressed and thereby the volume of etched region decreases, leading to the high-resolution fabrication.

4. Conclusions

High-quality ablation craters are successfully fabricated on a single-crystal GaN substrate by using wet-chemicals assisted fs laser ablation technique. By using high NA objective lens, the diameter of ablation crater decreases to as small as approximately 510 nm. It is expected that the fabrication resolution can be improved by using the second harmonic of the laser. This nano-fabrication technique of GaN is useful to form a variety of integrated microdevices, such as photonic crystals and so on. In addition, by using the wet-chemicals assisted fs laser ablation method, the debris is efficiently removed during and after the reaction in HCl solution, resulting in high quality processing. This advantage enables a successive fabrication of GaN using multiple pulses, so-called, laser direct writing, realizing fabrication of 3D micro structure inside GaN in the future.

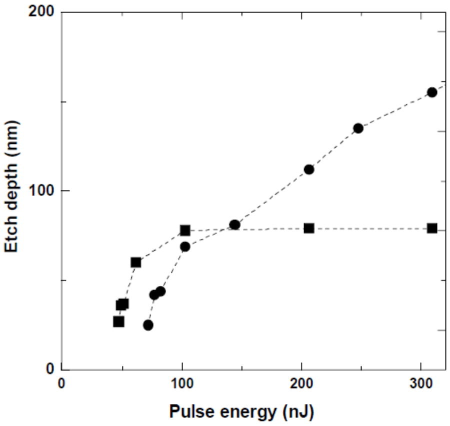

Fig. 4 Pulse energy dependence of etching depth for two-step processing method (●) and wet-chemicals assisted fs laser ablation (■).

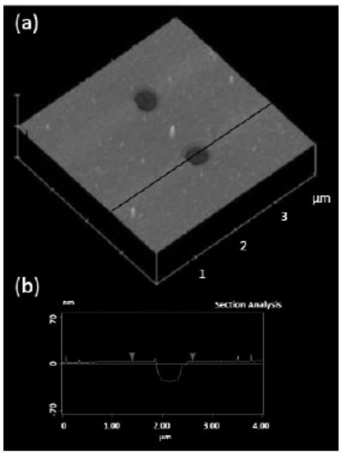

Fig. 5 AFM image of nano-scale crater formed by using wet-chemicals assisted fs laser ablation, the diameter of which is as small as 510 nm.

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