Fabrication of High-aspect-ratio Nanohole Arrays on GaN Surface by Using Wet-chemical-assisted Femtosecond Laser Ablation

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A periodic array of nanoholes with high aspect ratios was successfully fabricated by using a multi-scan laser irradiation technique, in which each position in the array is irradiated one time per scan with a femtosecond laser pulse. This technique can easily avoid interference to the laser pulses by micro-bubbles generated in the wet-chemical-assisted ablation process. As a result, we obtained nano-sized ablation holes with an aspect ratio of 1.6, which is much higher than that possible with single pulse ablation. The depth of the ablation craters formed by multi-scan irradiation technique was found to saturate at higher pulse number, presumably due to the limited depth of focus. We also revealed that the ablated depth strongly depends on the refractive index of the medium facing the GaN substrate. In fact, compared to ablation in air followed by HCl etching, the wet-chemical-assisted ablation process enhances the aspect ratio by about 30 % because of the high refractive index of the HCl solution. In addition, by controlling the synchronization of the laser pulses and the motion of the piezo-stage, an almost perfectly periodic arrangement of nanoholes was fabricated on the GaN substrate. The technique developed in this study is likely to make a significant contribution towards realization of two-dimensional photonic crystal structures on GaN-based blue light-emitting diodes.

DOI:10.2961/jlmn.2011.01.0004

Keywords: Femtosecond laser ablation, Wet-chemical process, Gallium nitride, Nanofabrication, High-aspect-ratio nanohole

1. Introduction

Development of a precise and efficient technique for fabricating nanostructures in wide band gap GaN is challenging issue because of the high thermal stability and chemical durability of the material. At present, electron beam lithography followed by plasma etching [1, 2] is commonly used to produce high-precision two-dimensional (2D) surface structures on GaN, and features as small as 150 nm have been fabricated. However, due to the complexity of the procedures, it suffers from high production costs and has low throughput, and is still difficult to implement in mass production. Although several other approaches have been studied, they do not offer further advantages over the electron beam lithography technique [3-6]. In contrast, laser ablation processes offer a different approach to micro/nanofabrication of GaN [7-9]. Recently we have developed a wet-chemical-assisted femtosecond (fs) laser ablation method and successfully fabricated nano-sized craters with a higher quality than with the conventional ablation by using the second-harmonic of near-infrared fs laser pulses [10, 11]. Since fs laser ablation is a direct and simple process, it is expected to be applicable to flexible fabrication of 2D periodic structures, allowing high efficiency and high throughput in production environment [12, 13]. This technique could even be applied to nanofabrication of GaN-based light-emitting diodes (LEDs). Such LEDs are widely used for many applications everywhere such as traffic lights, liquid crystal display backlighting, full color displays, and other general lighting purposes. At this time, however, blue LEDs suffer from the serious problem of low light extraction efficiency, which is attributable to a large amount of total internal reflection at the interface between GaN (n=2.5) and air (n=1). For example, the light extraction efficiency for a single GaN /air interface is less than 10 % despite the fact that the internal quantum efficiency of the LED is higher than 90 %. It has been proposed that integration of a 2D photonic crystal pattern of air holes on the device surface would be an effective means of enhancing the extraction efficiency [14-16]. In such a structure, total internal reflection is suppressed, and in-plane lateral guide modes of light are prohibited; the resulting vertical waveguiding effect increases photon emission in the off-plane direction. To maximize the effect of the photonic crystal structure, processing accuracy is of primary importance, since it is necessary to produce nanoholes with high aspect ratios. In the present study, we attempted to fabricate simple 2D photonic crystal structures consisting of arrays of high-aspect-ratio nanoholes using wet-chemical-assisted fs laser ablation. To achieve the required aspect ratio, multi-scan irradiation with a pulse-controlled fs-laser was carried out.

2. Experimental

The single-crystal GaN substrates (Kyma Technologies, Inc.) utilized in this work were 470 μm thick and exhibited n-type conduction. The chemically and mechanically polished Ga-face was subjected to the laser irradiation. We utilized an fs laser (Clark-MXR, CPA-2001) that emits pulses with widths of 150 fs [full width at half maximum (FWHM)], a wavelength of 387 nm (SHG) produced by a

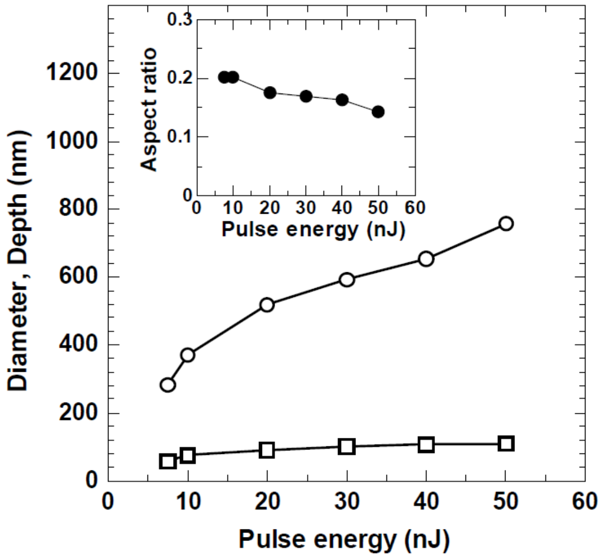

Fig. 1 Pulse energy dependence of diameter (○) and depth (□) in ablation craters formed by single-pulse irradiation using wet-chemical-assisted fs laser ablation. Inset is the variation of the aspect ratio (●).

BBO crystal, and a repetition rate of 1 kHz. A pulse picker integrated Pockels cell was used to control the repetition rate. The laser beam was collimated to a diameter of 3 mm and was then focused onto the substrate surface by a 100× microscope objective lens with a numerical aperture of 0.9 and with a working distance of 1.0 mm. We used two kinds of fabrication techniques. The first was wet-chemical-assisted fs laser ablation, in which the laser beam was focused directly onto a substrate immersed in a hydrochloric acid (HCl) solution. The thickness of the acid solution on the substrate surface was maintained at 630 μm. A two-step processing method, i. e., fs-laser irradiation in air followed by HCl treatment, was also carried out for comparison, although we have previously reported that this method was less suitable for high-quality fabrication than wet-chemical-assisted ablation [11]. The substrate was placed on an XYZ stage scanned by piezo actuators, which enables synchronization of the laser pulses with the stage, allowing the position of the irradiated spot to be precisely controlled. The characteristics of the ablation craters formed by the laser irradiation were investigated by atomic force microscopy (AFM), and cross-sectional profiles were used to determine the effect of irradiation conditions on the crater depths and FWHM diameters.

3. Results and discussions

Figure 1 shows the pulse-energy dependence of the depth and diameter of ablation craters formed by single-pulse irradiation using wet-chemical-assisted fs laser ablation. It can be seen that the diameter continuously increases with pulse energy, whereas the depth becomes saturated due to multiphoton absorption by the GaN [17]. Hence, the aspect ratio is limited to a maximum value of about 0.2 as shown in the inset of Fig. 1.

The lattice constants of photonic crystal structures are corresponding to the emission wavelength of LEDs; 470 nm for general blue LEDs. In addition, some reports suggested that enhancement of the light extraction efficiency

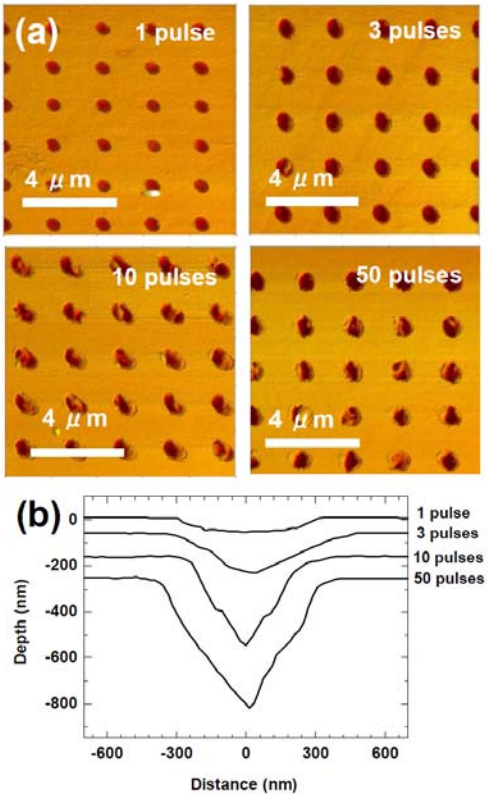

Fig. 2 (a) AFM images of nanohole arrays formed by multi-scan irradiation method using wet-chemical-assisted ablation in HCl solution at a pulse energy of 10 nJ for various pulse numbers, and (b) cross-sectional profiles of nanoholes for each pulse number.

was realized by the 2D arrays of nanoholes with the diameter of approximately 150 nm [2, 16]. In the case of a *p*-GaN layer with a thickness of 200 nm, the aspect ratio must then be greater than 1.3. Therefore, to increase the etched depth and thereby the aspect ratio, we employed multi-pulse ablation. The simplest methods would be to apply successive pulses to the same position, before moving the laser spot to the next position. The number of pulses could be controlled by changing the open time of the shutter. However, when the ablation reaction takes place in a liquid solution, which is the case for wet-chemical-assisted ablation, the micro-bubbles generated by the preceding pulses interfere with subsequent pulses, and the fabrication efficiency is drastically decreased. If the time interval between the pulses was longer than the time scale for disappearing of bubbles, such interference would be minimal. Although this could be achieved by using namely using a low repetition rate of pulses, the fabrication time would inevitably become much longer. To avoid this drawback, we developed a multi-scan irradiation technique, in which a series of sequential scans is performed and each position is irradiated with a single laser pulse during each scan. This provides sufficient time for the disappearance of micro-bubbles generated by the preceeding pulses due to self-pressurization effects, so that each pulse can successfully reach the substrate surface. In addition, high speed processing is feasible because, in principle, it is not necessary to decrease the repetition rate.

Figure 2(a) shows AFM images of nanohole arrays formed by multi-scan irradiation using wet-chemical-assisted ablation in a HCl solution at a pulse energy of 10 nJ. The number of scans, and hence the pulse number was 1, 3, 10 and 50, respectively. Pulse overlap at each position is well controlled due to the high positioning accuracy of the piezo stage. The cross-sectional profiles shown in Fig. 2(b) indicate that the ablated depth increases with pulse number, in strong contrast to the dependence on pulse energy for single-pulse ablation (Fig. 1). This implies that highly efficient fabrication can be achieved using the multi-scan irradiation method. In this case, the time interval between the scans was set to 40 second, which was sufficiently and much longer than the disappearance time of microbubbles. Although clarification of the disappearance time is so important, it is too difficult to measure it accurately at present, which is because of the low quality of monitoring image.

For comparison, Fig. 3 shows (a) AFM images and (b) cross-sectional profiles of nanohole arrays formed at the same pulse energy using the two-step processing method. The pulse-overlap accuracy appears to be quite high even for higher pulse number. In addition, the cross-sectional shapes are similar to those for wet-chemical-assisted ablation. This analogy between the two methods is not observed in the case of single-pulse ablation. Although the question of reason is still open at present, it is clear that the multi-scan irradiation method can significantly increase the ablation depth during either one-or two-step processing.

Figure 4 shows variations in hole diameter and depth as a function of pulse number for the wet-chemical-assisted

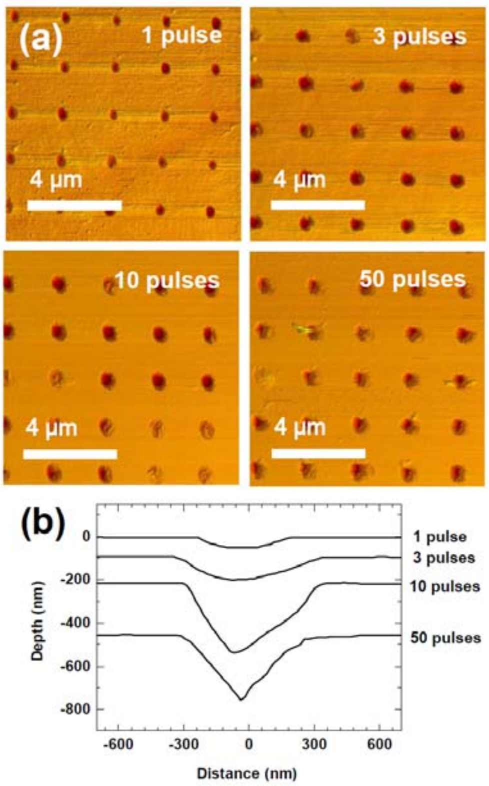

Fig. 3 (a) AFM images of nanohole arrays formed by multi-scan irradiation method using two-step processing method at a pulse energy of 10 nJ for various pulse numbers, and (b) cross-sectional profiles of nanoholes for each pulse number.

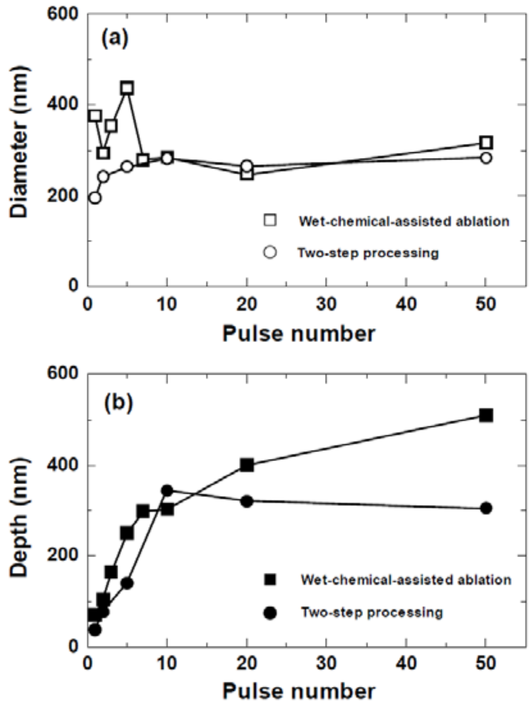

Fig. 4 Pulse number dependence of (a) diameter and (b) depth of nanoholes formed using the multi-scan irradiation method in the case of wet-chemical-assisted fs laser ablation (□ and ■) and two-step processing (○ and ●).

ablation and the two-step processing methods. In both cases, there seems to be very little dependence of the diameter on the pulse number. We speculate that thermal accumulation was minimized because of the pseudo-low-repetition-rate pulse. Meanwhile, the hole depth is seen to increase for pulse number up to 10 or 20, but then begins to saturate. It is interesting to note that the saturated depth at higher pulse number differs between the two methods.

In Fig. 5, the dependence of aspect ratio on the pulse number is plotted. For both methods, the aspect ratio is seen to initially increase and then become saturated at around 10 or 20 pulses, even though the depth and diameter have not been completely saturated yet. This indicates the similar ablation rates in both directions of diameter and

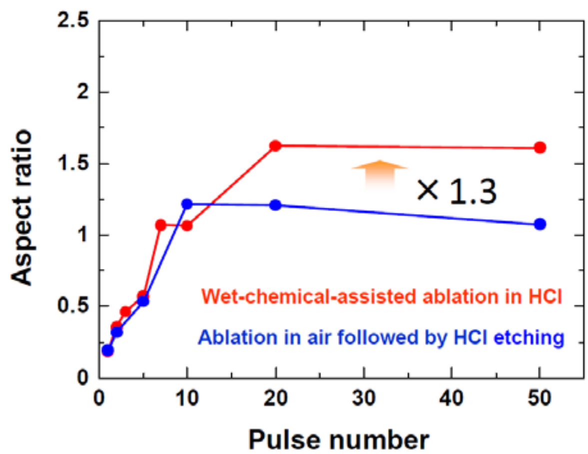

Fig. 5 Aspect ratios as a function of pulse number for the wet-chemical-assisted ablation (red closed circles) and two-step processing (blue closed circles).

depth. This is presumably due to the same intensity of incident beam at every point on the surface of an ablation crater, namely, bottom or lateral surface. The saturated ratios are 1.6 for wet-chemical-assisted ablation and 1.2 for the two-step process. These values are significantly higher than the best aspect ratio obtainable with single-pulse ablation. More notable is the fact that the saturated value for wet-chemical-assisted ablation is 30 % higher than that for ablation in air. This reason for this is thought to be the following. In the multi-scan irradiation method, when the first pulse irradiates the surface of the GaN substrate, an ablation reaction occurs just at the surface. Almost simultaneously, the Ga-rich phase remaining on the surface of the nano-crater is chemically removed by the acid solution. After a sufficient amount of time, the micro-bubbles disappear and the next laser pulse arrives in the subsequent scan. During the second pulse, ablation occurs at the new surface cropped out by the preceding ablation process. These steps are repeated for each subsequent scan. However, after 20 pulses or more, the ablation reaction progresses no further because the beam intensity at the bottom of the hole becomes smaller than the threshold intensity for ablation due to the limited depth of focus of the laser beam. Therefore, it is speculated that the final shape of the ablation hole after 20 pulses is determined by the spatial intensity distribution of the laser beam.

In the *r-z* coordinate system shown in Fig. 6, an incident laser beam with an intensity of I_0 is irradiated in the *z* direction and focused on the origin. If the intensity distribution of the incident laser beam along the *r* axis is described as Gaussian, the intensity at an arbitrary point, $I(r, z)$, can be expressed as

$$I(r,z) = I_0(z)\exp\left(-\frac{2r^2}{\omega(z)^2}\right) . \quad (1)$$

$I_0(z)$ denotes the intensity at the center of the beam and is calculated as $I_0(z) = 2I_0 / \pi\omega(z)^2$, where $\omega(z)$ is the beam

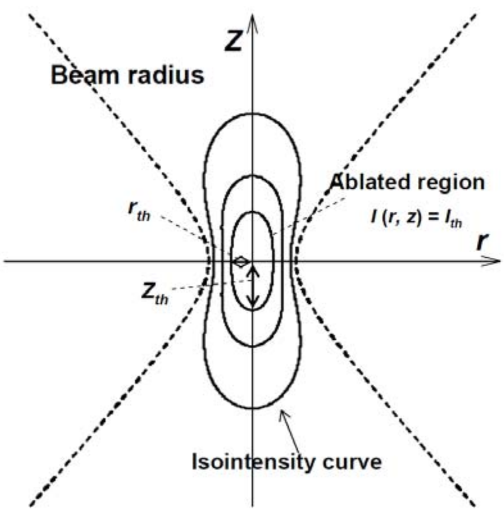

Fig. 6 Beam radius (dotted line) and isointensity curves for various intensities (solid lines). In particular, the isointensity curve for the ablation threshold intensity represents the ablated region formed by the multi-scan irradiation technique.

radius. Then, for any given intensity, the relationship between *z* and *r* can be obtained, leading to closed isointensity curves for different beam intensities, as shown in Fig. 6. At every point in this line, namely, bottom or lateral surface of ablation craters, the beam intensity is constant and ablation rate would be similar, as stated above. If the intensity is taken to be the ablation threshold intensity I_{th}, the obtained isointensity curve represents the ablated region produced by the multi-scan method as

$$r^2 = -\frac{\omega(z)^2}{2}\ln\frac{I_{th}\cdot\pi\omega(z)^2}{2I_0} . \quad (2)$$

By substituting the beam radius, $\omega(z) = \omega_0\sqrt{1+\left(Z^2/Z_R^2\right)}$, where Z_R represents the Rayleigh length and is expressed as $Z_R = \pi\omega_0{}^2 n/\lambda$, into equation (2), the depth Z_{th} and radius r_{th} of the ablation holes can be calculated as

$$Z_{th} = \frac{\pi\omega_0^2 n}{\lambda}\sqrt{\frac{2I_0}{\pi\omega_0^2 I_{th}} - 1} , \quad (3)$$

and $$r_{th} = \omega_0\sqrt{-\frac{1}{2}\ln\frac{\pi\omega_0^2 I_{th}}{2I_0}} . \quad (4)$$

It is interesting to note that while the depth depends on the refractive index, *n*, of the medium facing the GaN substrate, the radius is independent of this parameter. As a result, the aspect ratio strongly depends on the refractive index of the medium as

$$Aspect\ ratio = \frac{\pi\omega_0 n}{\lambda}\sqrt{\frac{2I_0}{\pi\omega_0^2 I_{th}} - 1} \Bigg/ \sqrt{-\frac{1}{2}\ln\frac{\pi\omega_0^2 I_{th}}{2I_0}} . \quad (5)$$

Based on the difference in the refractive index between air (~1) and HCl acid solution (~1.3), it can be estimated that a 30 % higher aspect ratio can be achieved with wet-chemical-assisted ablation than with the two-step processing method. This estimation agrees well with the experimental results.

At present, it is quite difficult to determine the threshold intensity of ablation accurately. As a preliminary calculation, we assume that the threshold is the minimum energy for ablation reaction. In the experiment using multi-scan irradiation method, the pulse energy is 10 nJ and the minimum energy is 7.5 nJ as can be seen in Fig. 1. Spot size, $2\omega_0$ is calculated using the equation, $\omega_0 = 0.61\cdot\lambda/NA\cdot M^2$. Since M^2 is 1.3, ω_0 would be 341 nm. From the equations (3)-(5), the diameter and depth can be estimated as 260 and 410 nm, indicating that the aspect ratio is 1.58. Although this estimation is not enough rigorous in terms of insufficiency of threshold estimation, the estimated values are very close to the experimental values.

4. Conclusions

For the purpose of producing a 2D photonic crystal on a GaN LED, we attempted to fabricate periodic arrays of high-aspect-ratio nanoholes on GaN substrates. By controlling the synchronization of the piezo-stage with the laser pulses, an almost perfectly tetragonal array of nanoholes was fabricated using wet-chemical-assisted fs laser ablation. Nanoholes with high aspect ratios (~1.6) were successfully produced using multi-scan irradiation method. This result clearly demonstrates that the multi-scan method is more suitable for fabrication of high-aspect-ratio nanoholes compared with the single-pulse ablation process. From a comparison with two-step processing method, we speculated that the intensity distribution of the focused laser beam determines the final shape of nanoholes formed by multi-scan irradiation. It was found that aspect ratio significantly depends on the refractive index of the medium facing the GaN substrate. This means that the use of an acid solution with a higher refractive index will lead to further enhancement of the aspect ratio.

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(Received: August 09, 2010, Accepted: December 21, 2010)