GaN ablation etching using short wavelength pulsed laser

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GaN ablative etching by KrF excimer laser and F_2 laser irradiation has been explored. Single pulse ablation using KrF excimer laser planarizes etched surface, however, multiple KrF irradiation roughens etched GaN surface significantly. Simultaneous co-irradiation of small fraction of F_2 laser in addition to KrF excimer laser effectively reduces surface roughness of etched GaN compared to the case of single-KrF excimer laser irradiation with multiple pulse. Irradiating delay time between both lasers is varied in order to investigate excitation mechanism as well as find optimum irradiation condition. More improved GaN surface is obtained with 40 ns-delayed irradiation of KrF excimer laser after the F_2 laser pulse, than in case of simultaneous irradiation.

Introduction

III-nitride semiconductor crystals (GaN, InN and AlN) and their alloys can cover a band-gap of 1.95–6.2 eV continuously, and practical utilize of high-brightness green and blue/violet light emitting diode (LED) is breaking out. Blue/violet laser diode (LD) is expected to be realized using III-nitrides, and it is promising for light source of ultra high-density optical storage. An etching process is indispensable for n-type Ohmic metallization of LED or LD structure grown on sapphire substrate, ridge fabrication of LD, and gate recess in GaN/AlGaN high electron mobility transistor (HEMT) operated under high temperature. Etching process is one of the essential process in device fabrication as well as other process such as cleaning, crystal growth, doping or metallization. Conventional etching for III nitride crystals such as plasma etching,[1,2] reactive ion etching (RIE)[3,4] or electrophotochemical etching[5] have difficulties in high-speed etching, which is mainly limited by their high hardness and high chemical stability, moreover, inducing defects is serious problem since its nature of high-energy contact process. Far different from those etching process, an ablative etching using high intensity short wavelength pulsed ns-laser can achieve high etching rate of ∼100 nm/pulse, preventing from defect introduction that arise yellow-orange emission in photoluminescence or electroluminescence.

In this paper, characterization of GaN ablative etching using KrF excimer laser will be presented, second, etching quality improvement by simultaneous irradiation of F_2 in addition to KrF excimer laser will be presented.

Experimental

Samples that we used were 700 nm-GaN:Mg, grown on c-plane sapphire substrate buffered by 10 nm-AlN using molecular beam epitaxy (MBE) equipping an RF cracking cell for nitrogen source. Ni mesh with plenty of 25 μm square holes was set on the samples as a contact mask for micropatterning before the irradiation. The etching process was consisted of laser ablation and successive hydrochloric acid treatment. A KrF excimer laser ($\lambda = 248$ nm, FWHM = 34 ns, Lambda Physik LPX 205i) and an F_2 laser ($\lambda = 157.6$ nm, FWHM = 20 ns, Lambda Physik LPF 105i) were used for laser ablation. The experimental setup is shown in Fig. 1. Both lasers were triggered by a digital pulse generator (Stanford Research Systems DG-535). The F_2 laser was introduced thorough an nitrogen purged section. The KrF excimer laser was introduced from outside of the ambient controlled section. Coaxial irradiation of both lasers was realized by using dichroic mirror based on MgF_2 substrate, that not only reflects KrF excimer laser but also transmits F_2 laser. Fluence of F_2 laser was varied from 0.06 to 0.2 J/cm^2 by inserting/discarding thin fused silica substrate indicated as attenuator in Fig. 1. Fluence of the KrF excimer laser is varied up to 3.5 J/cm^2 for single wavelength irradiation. For the case of two-laser irradiation, it was varied from 1.0 to 1.34 J/cm^2. Pulse arrivals of both lasers were monitored by Si-PIN photodetector. Delay time of F_2 laser pulse arrival between KrF excimer laser pulse arrival (Δt) was varied in ± 1 μs range. In order to investigate influence of F_2 laser addition to KrF excimer laser irradiation, single-KrF irradiation was also done with laser intensity corresponding to total intensity of two lasers for the case of simultaneous (semi-simultaneous) irradiation. Etched depth (z) was measured using stylus profiler. Surface morphology was observed using a conventional opti-

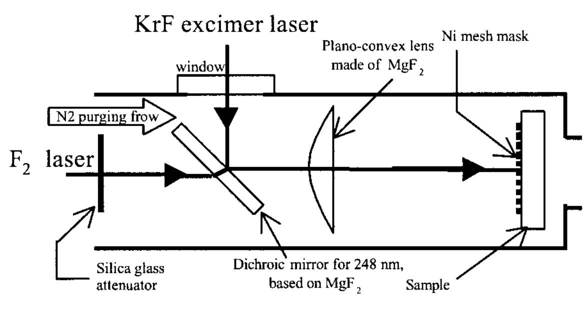

Fig. 1. Schematic diagram of the irradiation configuration.

cal microscope and a scanning electron microscope (SEM).

Results and discussion

KrF excimer laser ablation etching

GaN ablation takes place beyond the ablation threshold, and as-ablated surface exhibits metallic color and soft surface with cracks and pits. Ga3d x-ray photoelectron spectroscopy (XPS) results revealed that the as-ablated surface had Ga-rich off-stoichiometric composition, and the Ga-rich layer was removed by 5-min hydrochloric acid treatment.[6)]

Figure 2 shows laser fluence (F_{KrF}) dependence of etching rate for the case of a single pulse irradiation. High etching rate of ~135 nm/pulse was attained at 3.5 J/cm^2. The etching rate acceleration is apparent beyond 1.2 J/cm^2. Since GaN has band-gap (E_g) of 3.45 eV at room temperature and electron affinity (χ) of 4.15 eV, direct photoionization, i.e., photonic bond breaking requires 7.6 eV. Therefore, single photon of KrF excimer laser (4.99 eV) is insufficient for direct bond breaking in this material. Most of electron which once excited from valence band to conduction band is thought to be relaxed to valence band, results in temperature rise. Thus, pyrolysis reaction may become dominant, and the etching rate shows nonlinear increase for logarithm of laser fluence.

Laser fluence (F_{KrF}) dependence of average roughness (R_a) measured after the single-pulse irradiation and the chemical treatment is shown in Fig. 3. The R_a is evaluated in 5 μm square area of etched area. R_a is reduced with the increase of laser fluence. The R_a is lowered to ~3.3 nm (i.e., 52% reduction) with F_{KrF} beyond ~1.5 J/cm^2. We regard that the planarization effect is caused by lateral heat conduction in Ga-rich layer formed during/just after the laser irradiation. Since the Ga-rich layer has smaller heat conductivity compared to GaN crystal, the Ga-rich layer thought to confine and disperse the heat inside itself, and results in averaging of the roughness at the interface of the Ga-rich layer and unmodified GaN. Thus, higher intensity where the heat effect is significant causes surface planarization.

Figure 4 shows variations of z as a function of the number of pulses (n) for various F_{KrF}. The etching depth turned out to

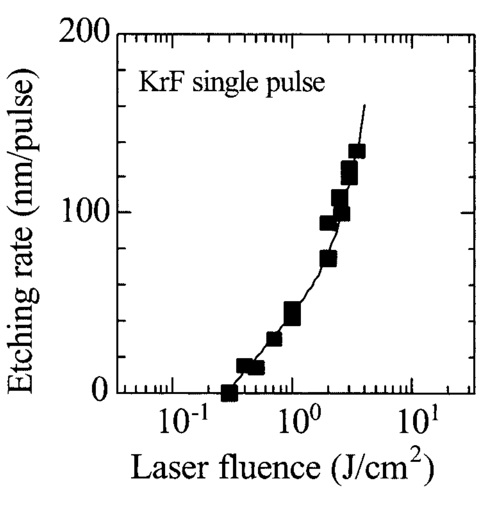

Fig. 2. F_{KrF} dependence of etching rate. The number of irradiated pulse is 1.

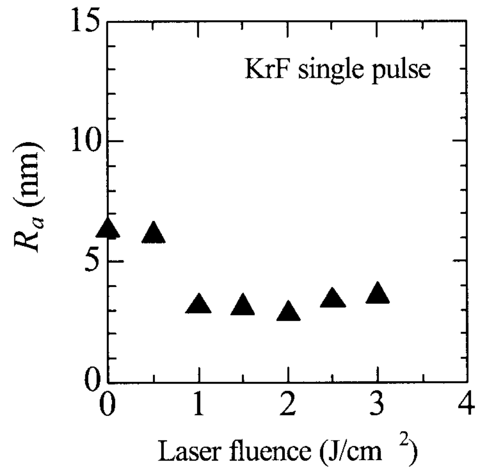

Fig. 3. F_{KrF} dependence of the R_a. The number of irradiated pulse is 1.

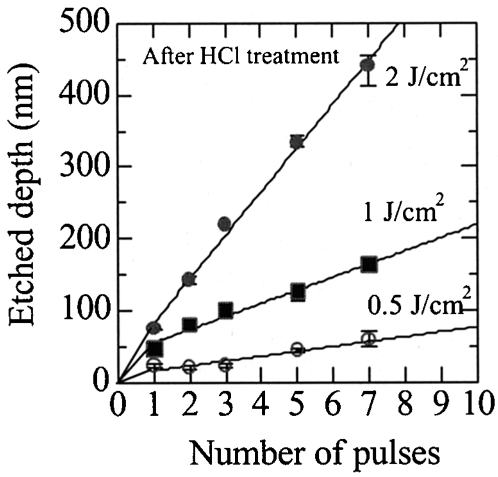

Fig. 4. Relation between the total etched depth z and the number of pulses n.

be controlled by either of F_{KrF} and n. The slopes indicated in Fig. 4 mean etching depth per pulse (etching rate), and the variation of the slopes between less and more than $n = 1$ can be seen in this figure. Larger reflectivity and absorbance of the Ga-rich surface formed by the first pulse decrease the etching rate (nm/pulse) for further pulses.

As we mentioned above, an increase of the laser fluence decreases microroughness of chemically treated GaN surface as for single-pulse ablated sample, however, multiple-pulse irradiation causes significant surface roughening. A domed structure is formed on the sample irradiated with 5 pulse KrF irradiation, and the chemical treatment can not remove this structure, as shown in Fig. 5 (a).

Ablation etching by co-irradiation of F_2 in addition to KrF excimer laser

Geometrical improvement has been reported using combination of ultra violet (UV) (Nd:YAG 4ω: $\lambda = 266$ nm) and vacuum ultraviolet (VUV) (H_2 Raman laser: $\lambda = 133$–184 nm) pumped by 266 nm, for hard materials.[7] In order to improve the surface roughness of GaN in the case of multiple pulse irradiation, we employ F_2 laser for co-irradiation with KrF excimer laser, that enables more flexible control of laser intensity and irradiation timing (simultaneous or delayed, compared with the prior work [7]). In our former work, etching threshold fluence of F_2 laser and KrF excimer laser were turned out to be $0.2\,J/cm^2$ and $0.3\,J/cm^2$, respectively.[8] We set the F_2 laser fluence below the etching threshold for the case of two-laser irradiation.

Figures 5 (a)–(e) are SEM images taken from 5 pulse irradiated samples, after the chemical treatment. Figures 5 (a)–(c) are taken from single-KrF irradiated samples. The fluences for single-KrF irradiated samples are (a) $1.0\,J/cm^2$, (b) $1.1\,J/cm^2$, and (c) $1.34\,J/cm^2$. The KrF fluence is fixed at $1.0\,J/cm^2$ for simultaneous two-laser irradiation. The fluences of the additional F_2 laser are (d) $0.12\,J/cm^2$, and (e) $0.2\,J/cm^2$. For the case of single-KrF etching, a domed structure on the etched surface can not be taken away by the increase of laser fluence. Such surface roughening is thought to be sign of pulse-to-pulse roughening accumulation. While for the case of two-laser simultaneous irradiation ((d) and (e)), as the increase of F_2 laser fluence, etched surface is planarized. The planarization effect is reflection of the temperature rise caused by the KrF excimer laser irradiation. In the simultaneous irradiation regime, increase in F_2 laser fluence may causes increase in absorption coefficient for KrF excimer laser, and this results in decrease of etching depth.[9] Therefore, the KrF excimer laser beam is absorbed in shallower region with the assistance of simultaneous F_2 laser irradiation, read to tight confinement of heat, results in planarization of etched surface.

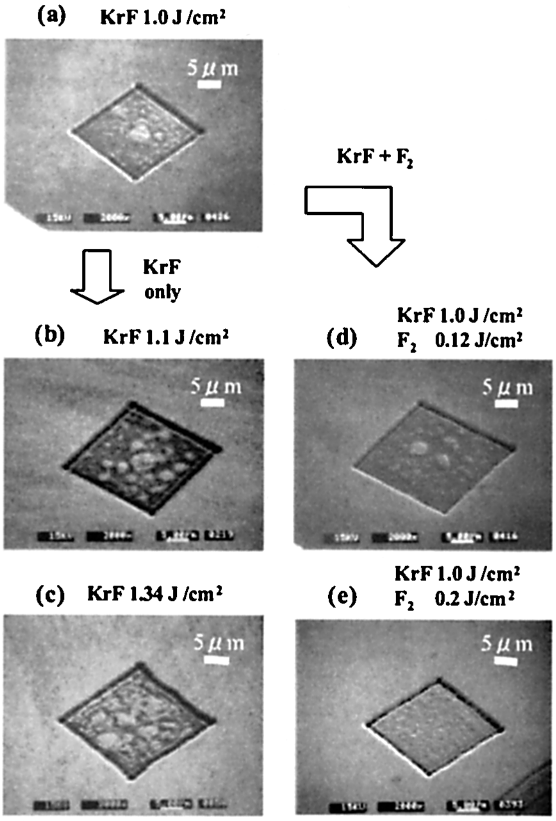

Fig. 5. SEM micrograph of KrF etched samples ((a)–(c)), and two-laser irradiated samples ((d) and (e)). The number of irradiated pulses is 5.

Δt dependence of the etched depth is shown in Fig. 6. The number of irradiated pulses is 5. The fluences of KrF excimer laser and F_2 laser are $1.0\,J/cm^2$ and $0.19\,J/cm^2$, respectively. Δt below 0 means that KrF excimer laser pulse arrives before F_2 laser pulse arrives, Δt above 0 means opposite irradiation sequence of former one. Priority arrival of etchable KrF pulse (Δt below 0) causes surface ablation as well as formation of highly Ga-enriched layer at the ablated surface, which has high reflectivity and absorbance. Since sequentially irradiated F_2 laser is non-etchable, it causes almost no etching depth increase. While, for the opposite sequence (F_2 laser pulse followed by KrF laser pluse), prior-arrived F_2 laser pulse affect no ablation but may cause slight modiacation, that lowers ablation threshold for sequential KrF excimer laser pulse. Therefore, the depth etched by the latter irradiating sequence is deeper than that etched by the former irradiating sequence. The etching depth shows maximum value around Δt of 40 ns. Around this Δt region, two lasers are thought to be absorbed into GaN crystal before surface reflectivity change, and some special electron excitation process may takes place. 7.9 eV-photon of F_2 laser has potential of direct photoionization in GaN. F_2 laser irradiation not only generates defect such as N vacancy, whose energy level is near the conduction band edge in the band gap, but also generates free carriers. The generated electrons are supposed to be trapped by such defects, and sequentially arrived KrF-photon excites the electrons beyond the vacuum level results in dissociation of Ga-N bonding. The generated defects are metastable, however, trapped electrons have certain lifetime. We regard that the sequential KrF-photon should be irradiated before the trapped electrons relax to the valence band. Thus, the ~40 ns-delayed KrF photon arrival provides best matching for excitation of trapped electron generated by the prior-F_2 laser irradiation.

Figures 7 (a)–(d) are SEM images taken from two-laser irradiated samples with Δt of (a) -200 ns, (b) 0 ns, (c) 40 ns, and (d) 200 ns. The fluences of KrF excimer laser and F_2 laser are $1.0\,J/cm^2$ and $0.19\,J/cm^2$, respectively. The n is 5.

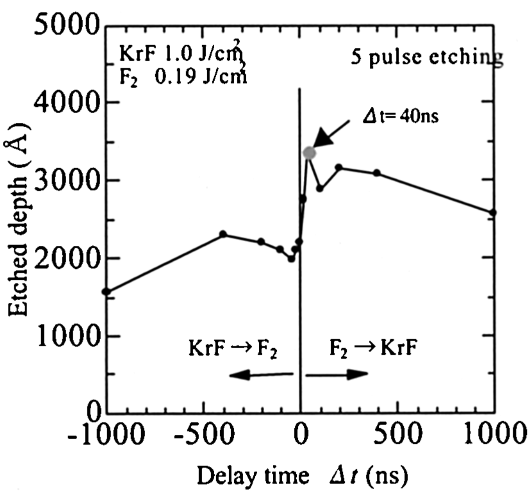

Fig. 6. Δt dependence of the etched depth.The number of irradiated pulses is 5.

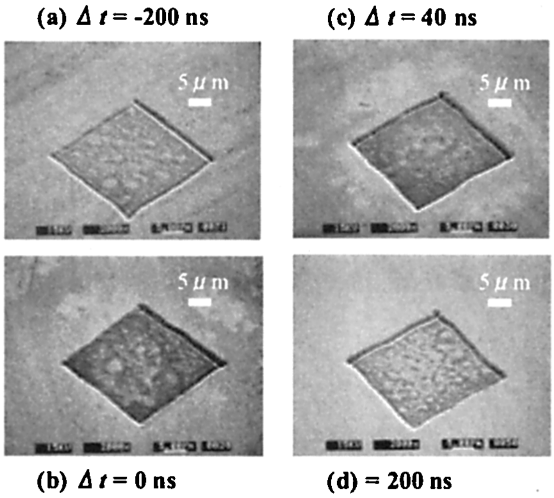

Fig. 7. SEM micrographs of samples etched with (a) $\Delta t = -200$ ns, (b) 0 ns, (c) 40 ns, (d) 200 ns. The number of irradiated pulses is 5. The fluences of KrF excimer laser and F_2 laser are 1.0 J/cm^2 and 0.19 J/cm^2, respectively.

In this SEM observation, we found most planarized etched surface in the sample irradiated with $\Delta t = 40$ ns (Fig. 7 (c)), but not in $\Delta t = 0$ ns (Fig. 7 (b)). The etched depth of the sample irradiated with $\Delta t = 40$ ns is 340 nm. We regard that the beforementioned coupled excitation realizes efficient photoionization of crystal, read to improved quality ablation etching.

Conclusion

Multiple KrF excimer laser irradiation roughens etched surface significantly, that is serious problem in deep etching of GaN, however, simultaneous coaxial irradiation of F_2 laser in addition to KrF excimer laser improves etched surface quality. Delayed KrF-photon irradiation is thought to be suitable for sequential efficient excitation of electron before they relax, they are trapped by the defects generated by prior-irradiated F_2 photon. Most improved etching surface is obtained by the 40 ns-delayed KrF irradiation, at which highest etching depth is achieved.

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