CTuM32 Fig. 2. Single-mode tuning characteristics of a standard diode laser (Hitachi HL 6720G) without an external cavity (black dots) and with a piezo-driven external cavity (squares).

μm by proper setting the temperature of the diode lasers and the one of the nonlinear crystal. The MIR laser power is typically $P_{\text{DFG}} = 0.2 \mu\text{W}$. Details of the laser system are described in Ref. 1.

The use of diode lasers as signal and pump sources for the DFG process limits the tuning range of accessible wavelengths in the MIR. There are several wavelengths within the gain profile of a diode laser, for which a single-mode operation is not possible. The black dots in Fig. 2 indicate the wavelength ranges for single-mode operation of a standard diode laser (Hitachi HL 6720G). Unfortunately, this characteristic mode jump behavior is different for each diode laser. However, the tuning characteristics of diode lasers can be improved very easily when an external short cavity around the laser is used.² In that case a glass plate is mounted on a piezo and is fixed close to the diode laser output ($d < 100 \mu\text{m}$) to form an external cavity. By changing the reflectivity of the glass plate and the external-cavity length when applying different piezo voltages, the mode structure of the diode laser is modified. Results of such measurements are shown in Fig. 2 (squares). In that case all wavelengths in the spectral range between 672 and 677 nm are covered by single-mode operation. This improves the tuning characteristics of a MIR-DFG diode laser system significantly. First results of extended tuning possibilities in the MIR are reported.

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CTuM33

Deep ultraviolet enhanced wet chemical oxidation and etching of gallium nitride

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Etching of III-V nitrides has become an important processing technique for realizing short-

CTuM33 Fig. 1. EDX analysis of the as-grown and the UV-illuminated GaN samples.

wavelength emitters, detectors, and high-temperature electronic devices. Due to the chemical stability of III-V nitrides, current practice has instead pursued the dry-etching techniques. However, great challenges remain to reduce surface damage and increase layer selectivity in the plasma dry etching and to increase the etch rate in excimer-assisted dry etching. Ultraviolet (UV)-assisted photochemical wet etching of nitrides,¹ on the other hand, presents a promising alternative to solve these problems. In this work, we present a use of deep UV irradiation to enhance the oxidative-dissolution process in the photo-electrochemical (PEC) etching of gallium nitride (GaN). Our study indicates that the hydration effect plays an important role in establishing a peak etch rate as high as 90 nm/min. and 120 nm/min. in aqueous potassium hydroxide (KOH) and phosphorus acid (H_3PO_4) solutions at $\text{pH} = 14.25$ and 0.75, respectively.

The unintentionally doped MOCVD grown GaN samples were measured to be n type with a carrier concentration of 10^{17} cm^{-3} and a thickness of 4 μm . To facilitate the PEC etching, a 253.7-nm Hg line source emitting at an intensity of 10 mW/cm^2 was used. The galvanic PEC cell was constructed by immersing a GaN working electrode, a Pt counter electrode, and a saturated KCl calomel reference electrode in the electrolyte. The PEC etching experiments were conducted at room temperature without external bias.

In Fig. 1 we compare the energy-dispersion x-ray analysis (EDX) data of the as-grown GaN sample with that under a UV-illumination in a dilute H_3PO_4 electrolyte of $\text{pH} = 3$. The dramatic increase of oxygen counts in the latter clearly indicates a rich oxide content. From an x-ray diffraction (XRD) analysis we identify the peaks at $2\theta = 34.46^\circ$ and 72.74° to the diffraction from $\beta\text{-Ga}_2\text{O}_3$ (111) and (222), respectively. The observation of UV-enhanced oxidation of GaN elucidates a promising consequence for wet chemical etching of GaN. In Fig. 2 we show the SEM micrograph of a PEC etched GaN sample with a total etch depth $\sim 2 \mu\text{m}$. The vertical striations shown in the side-wall are due to the striations in the metal mask that were transferred into the GaN feature during the etch. With optimization of the masking process, the anisotropic PEC etching on GaN can yield smooth side-walls and enable etched laser facets.

We illustrate in Fig. 3 the pH dependence of the normalized GaN PEC etch rate in aqueous KOH solutions. A hydration model analysis of $R = C \cdot [\text{H}_2\text{O}]^r [\text{OH}^-]^s$ indicates the peaking

CTuM33 Fig. 2. SEM micrograph of a PEC etched GaN sample.

CTuM33 Fig. 3. A hydration analysis of the PEC etch rate. A mean hydration number $n_h = 5$ was used for KOH in the analysis.

effect is due to a competition between the free water molecules (H_2O)_f and the hydroxyl ions (OH^-). In order to characterize the rapid variation of GaN etch rate at $\text{pH} > 14$ and the slowly falling tail in the dilute pH regime, two independent sets of exponents (r, s) = (15, 3) and (20, 0.5), respectively, are used in the analysis. These two sets of fitting parameters enclose the subtleties of the rate-limiting mechanism and are subjected to further investigation.

In summary, we have demonstrated a deep UV-enhanced oxidation and etching process on GaN. A hydration model analysis on the KOH-based PEC etch rate indicates the peaking effect is due to a competition between the (H_2O)_f and OH^- .

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CTuM34

Semiconductor material process with UV laser irradiation

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In this paper, we present our results of using UV laser for processing silicon and GaAs. The laser source is the fourth harmonic (266 nm) of a Q-switched Nd:YAG laser. This laser source is highly coherent so that interference fringe can be easily formed. We have used a

prism to form interference fringe for directly ablating gratings on the surface of silicon, GaAs, GaN, and LiNbO₃. Such gratings can find many applications such as laser-cavity feedback and temperature sensing. Here, we discuss the responses of those materials to the laser irradiation.

We have found that a silicon substrate re-

CTuM34 Fig. 1. AFM picture of a silicon grating fabricated with 7-mJ laser pulses.

CTuM34 Fig. 2. AFM picture of a silicon grating fabricated with 19-mJ laser pulses.

CTuM34 Fig. 3. FTIR spectra of 6 silicon samples irradiated with different laser wavelengths and power levels.

sponded differently with different laser power levels. Figures 1 and 2 are the atomic force microscopy (AFM) pictures used to show the difference between the samples fabricated with medium and high laser power values. The sample in Figs. 1 and 2 was made with 7 and 19 mJ pulse energy, respectively. It can be seen that with the relatively low laser energy, cotton-shape material was produced to form the crests of the grating (Fig. 1). This material was determined to be silicon oxide. Silicon oxide can be removed with HF etching. It was found that after HF dip, the crest positions of the grating became valleys. The reaction is hypothesized as follows: After silicon absorbed photons for heat, the silicon was not only melted but also oxidized. The silicon oxide stayed at the same position of melting and formed the crests of the corrugation because silicon oxide had a larger volume than silicon. On the other hand, a very regular grating shape was formed when a silicon substrate was illu-

minated with a higher power, as shown in Fig. 2. In this case, little silicon oxide existed on the surface. It implied that either silicon or the produced silicon oxide was evaporated under the illumination of the high power. We have also studied the composition of the silicon oxide with Fourier-transform infrared (FTIR) spectrometer measurements. Figure 3 shows the FTIR spectra of the silicon oxide from six samples. Three of them were fabricated with a 266-nm laser and the other three were made with a 532-nm laser. Different process conditions are given in the figure. The dip for all samples near 1075 cm⁻¹ represents the existence of SiO₂. It is noted that other oxide composition exists, as indicated by the curve suppression in the range from 1125 to 1250 cm⁻¹. It is estimated that the dielectric constant of this oxide is 6.3. The silicon oxide composition produced under different environmental conditions and laser power levels will be discussed.

III-V compounds such as GaAs respond to laser illumination in a different way. Typically, the crests of the gratings formed on a GaAs substrate are quite sharp. However, after it was dipped in a HCl solution for removing Ga, the crest peaks became smoother. From the results, we can hypothesize the process of forming GaAs grating as follows: The absorbed photons generate heat, which is high enough for breaking the GaAs bond. Then, As is evaporated and solid Ga is sputtered by photon pressure away from the valleys of the periodical corrugation.

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CTuM35

Laser ablation time-of-flight mass spectrometric diagnosis of the surface states of porous siliceous materials

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Zeolites and related siliceous porous solids are widely used in industrial sorptive, ion-exchange, and catalytic processes in which the effects of the inner surface states on the properties are important from both the practical and theoretical interests. In this paper, a novel surface diagnostic technique based on laser-induced cluster generation will be reported.

Laser ablation has widely used for the efficient generation of atomic and molecular clusters. We have performed the mass spectrometric study of cluster generation from high silica porous siliceous materials by XeCl excimer laser ablation time-of-flight mass spectrometry (TOF-MS). Several cluster sequences [(SiO₂)_nX]⁻ with different X were observed. It is interesting to find that the compositions of the cluster sequences (i.e., X) and the abundance distributions are closely related to the surface states of the samples. The most prominent result is the effect of surface silanol group (SiOH) on the cluster formation. For the typical mass spectra of surface SiOH containing samples, five cluster sequences of [(SiO₂)_n]⁻,