Dry Etching of GaN/InGaN Multiquantum Wells Using Inductively Coupled Cl₂/CH₄/H₂/Ar Plasma

Ji-Myon Lee,* Sang-Woo Kim, and Seong-Ju Park

Department of Materials Science and Engineering and Center for Optoelectronic Materials Research, Kwangju Institute of Science and Technology, Kwangju 500-712, Korea

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The dry etching of nitride semiconductors represents a key technological step in the fabrication of optoelectronic devices, as well as the integration of high-speed electronic circuits. For optoelectronic and waveguiding applications, a higher retention of surface morphology and smooth sidewalls are required. In addition, the fabrication of nitride-based optoelectronic device, such as laser diodes involves the use of a laser cavity, which is formed by an etching, and epilayer regrowth technique on the etched areas. Therefore, the etched surfaces and sidewalls must be free of virtually all contamination, defects, and redeposits. To meet these requirements, numerous reports on the use of dry etching techniques have been reported such as reactive ion etching (RIE), chemically assisted ion beam etching (CAIBE), high density plasma etching using electron cyclotron resonance (ECR), and inductively coupled plasma (ICP) etching. However, it is noteworthy that most of the previous studies were focused on the etching of single GaN or InN film, in order to investigate the etch characteristics of these nitride layers. In terms of the etching of InN or InGaN, Cl radicals react with In to form a nonvolatile InCl₃. In the case of laser diodes where In-containing compounds are used as an active layer, it is highly desirable to etch the layers at the same etch rate, i.e., nonselective etching, which leads to a featureless, smooth, and vertical etched side. Thus, the removal of In-containing compounds is very important because their presence can cause a roughening of the etched surface, thus decreasing the optical performance of the device. However, the dry etching of GaN/InGaN-based heterostructures is not a subject that has been extensively investigated to date.

In this paper, we report on the ICP etching of multiple quantum well (MQW) structures containing InGaN as an active layer as well as the effect of surface properties by using a Cl₂/CH₄/H₂/Ar plasma chemistry. The effects of ICP source power, and rf table power on the etch rate, the surface, and sidewall morphology were investigated. The effects of etching on the electrical properties of the etched GaN surface are also discussed here.

Experimental

Undoped 1.5 μm thick GaN and 0.3 μm thick In₀.₁₂Ga₀.₈₈N epi layers were grown on a c plane sapphire substrate by metalorganic chemical vapor deposition (MOCVD). The layer growth sequence of the MQW on the sapphire substrate was as follows: a GaN nucleation layer, an n-GaN, seven periods of In₀.₁₂Ga₀.₈₈N/GaN multiple quantum well, and an undoped GaN or a p-type GaN capping layer. A detailed description of growth procedures was provided in previous papers.

An ICP reactor, equipped with a 3 kW ICP power supply, was connected to a load-lock chamber. The dc bias voltages were provided by superimposing an rf bias (13.56 MHz) on the sample. A 7×7×7 mm sample was used for etch rate measurement. For the optical emission spectra (OES) measurement, a complete wafer with a diameter of 2 in. was used to increase the OES signal since the OES signal intensities are directly proportional to the sample size. Samples were mounted on an anodized Al carrier that was clamped to a cathode and back side cooled with He gas. Detailed descriptions of sample preparation procedures are reported in our previous paper. The etch conditions used in this study were: 30 sccm Cl₂, 8 sccm H₂, 16 sccm Ar, 10 mTorr pressure, 500-2000 W ICP power, 100-250 W rf power, and a 20°C table temperature. The CH₄ gas was added to the plasma in order to etch the In-containing compound. SiO₂ with a thickness of 1 μm was deposited on the sample as a mask layer by plasma-enhanced chemical vapor deposition (PECVD), and patterned using a carbon-based photoresist (PR). After PR lithography, the SiO₂ mask was patterned with a buffered oxide etchant (BOE), and finally, the PR was removed using acetone prior to ICP etching. The SiO₂ mask was stripped away with a buffered HF solution after the plasma etching process. During the etching process, the plasma was monitored by OES and the etching was simultaneously monitored by a laser interferometer using a 6783 Å laser. Etch rates were estimated from the depth profile measurements with a surface profilometer after removing the SiO₂ mask using a BOE solution, and these data were compared to the results of the oscillation signal of a laser interferometer. The anisotropy and the sidewall morphologies were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). To investigate the effects of a dry etch on the electrical properties of GaN, Schottky diodes were fabricated using Ni/Au (30/80 nm) as Schottky-metals and Ti/Au (30/80 nm) as ohmic-metals, and the reverse current-voltage characteristics of diodes were measured.

Results and Discussion

Figure 1 shows the etch rates of (a) GaN and (b) InGaN as a function of ICP power in Cl₂/CH₄/H₂/Ar plasma. Although the rf table power was held at 100 W, the induced dc bias was decreased from −185 to −25 V with increasing ICP power. This is due to the higher plasma density which suppresses the cathode dc bias at a higher ICP power. The etch rate of GaN was increased with increasing ICP power due to an increase in the density of active etchant species, as reported in our previous study. It is also noteworthy that etch products of Ga, as such as GaCl₃ and Ga(CH₃)₃, are

* Electrochemical Society Student Member.
* E-mail: sjpark@kjist.ac.kr

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known to be highly volatile. These results suggest that the etching mechanism of GaN under these etching conditions is a reactant-limited process, which is very similar to the results in the literature. However, the InGaN etch rate was increased with increasing ICP power up to 1000 W, but was saturated above 1000 W of ICP power. Shul et al. reported a dry etching of InN using Cl₂/CH₄/H₂/Ar plasma chemistry at high temperatures. They observed a drastic increase in the etch rate of InN above 150°C and proposed that the surface reaction kinetics became dominant at high temperatures above 150°C. Their results suggest that, at temperatures below 150°C, the surface reaction mechanism is rather a rate-limiting process in the etching of InN. In other words, even though the mass transfer of the active radical is increased with increasing ICP power, the etching can be limited by a surface reaction such as the formation of a low volatile etch product and/or the desorption of an etch product from the surface at low temperatures. That is, the etching process of InGaN in this study is no longer reactant-limited above the 1000 W of ICP power. Rather, surface reactions, such as the ion-assisted removal of In or InCl₅ may limit the etching process.

In order to investigate the effect of plasma chemistry on the etch characteristics of an MQW structure, we monitored the intensity of an in situ interferometric reflection during plasma etching at an ICP power of 1000 W. It is noteworthy that the etch rates of GaN and InGaN are almost the same at 1000 W of ICP power. As shown in Fig. 2a, the smooth oscillation of interferometric signal indicates that a non-selective etching of the MQW was progressively performed with increasing etching time by a Cl₂/CH₄/H₂/Ar plasma. However, when the MQW sample was etched by Cl₂/H₂/Ar plasma, a slight time delay in the constructive interference was observed, as indicated by the arrow in Fig. 2b. This delay of interferometric signal can be seen since the Cl₂-based plasma is not able to readily etch InGaN due to the formation of nonvolatile etch product, such as InCl₅. This result indicates that the etch rate of MQW samples by a Cl₂/H₂/Ar plasma is not uniform due to the presence of InGaN layers in the MQW.

Figure 3 shows the emission spectrum of a Cl₂/CH₄/H₂/Ar discharge with the MQW sample being etched at 1000 W of ICP power and 200 W of rf power. In this experiment, a complete MQW sample was used, in order to identify the etch products by increasing the OES signal intensity. As shown in Fig. 3, the intense atomic H (434 nm) and CH (330-342 nm) lines are detectable during the etching of MQW. The emission lines of atomic Ga (403, 417 nm), In (325, 410 nm), and GaCl (330-342 nm) which originate from the etch products of GaCl₅, can be also observed in the OES spectra. While the Ga and the GaCl emission peaks corresponding to the etch products could be seen in the OES spectrum, only the atomic In peak was observed for the In-related etch product. It is noteworthy that InCl₅ or In(CH₃)₃ peak was not observed in the emission spectra, probably due to the low concentration of In. Another possible explanation for the lack of InCl₅ or In(CH₃)₃ in the spectra involves that the redecomposition of the etch products in the plasma, as suggested by the Feurprier et al. In addition, an N₂ emission line at 358 nm from the etch product of nitrogen from nitrides was not observed. Instead, a CN spectral line at 389 nm that originates from the reaction of CH and N₂.
(CH₄⁺ + N₂⁺ → CN + N + H₂ + Hₑ + e)\(^1\) was observed in this study.

Figure 4 shows etch rates for GaN and MQW and the dc bias of the MQW etched as a function of rf power in the Cl₂/CH₄/H₂/Ar (20% of CH₄ concentration) plasma. The etch rate of the MQW increased with increasing dc bias, induced by rf power, and the etch behavior was similar to that of GaN, suggesting that the removal of In is not a rate-limiting step under these etch conditions. The etch rate of the MQW was slightly larger than that of GaN at a higher rf power, probably due to the lower bonding energy of In-N (7.72 eV/atom) compared to that of Ga-N (8.92 eV/atom).

Figure 5 shows the SEM images of the MQW etched without CH₄ (a) and with 20% CH₄ (b) at 1000 W of ICP and 100 W of rf power. The SiO₂ mask was removed prior to the SEM measurement. As shown in Fig. 5a and b, a high anisotropy of the etch profile was observed, irrespective of the use of CH₄ in the plasma. However, the morphology of the etched bottom surface was severely degraded by the residues when the MQW was etched in the absence of CH₄ (Fig. 5a), compared to that etched using CH₄ (Fig. 5b). An AFM measurement of the etched surface showed that the root-mean-square (rms) roughness of the MQW sample etched with a Cl₂/H₂/Ar plasma was typically about 10-15 nm, while that of the sample etched with a Cl₂/CH₄/H₂/Ar plasma was as small as 5 nm. Furthermore, the sidewalls of the buried InGaN MQW layer were heavily grooved in the vertical direction and appear to be different from the striations which are derived from mask irregularities. From these results, we conclude that the formation of residue on the etched surface is caused by the micromasking effect of the InGaN layer, which was not etched away by the Cl₂ plasma.

In addition, we investigated the diode characteristics of the Schottky contact, which was fabricated on the dry etched surface, and which is known to be highly sensitive to etch-induced defects.\(^2\) Figure 6 shows the reverse current-voltage (I-V) characteristics of a GaN Schottky diode. While the as-grown sample (Fig. 6a) showed rectifying contact behavior, the reverse I-V of an etched GaN exhibited severe degradation,\(^3\) as shown in Fig. 6b. However, the I-V characteristics were significantly improved when the sample was annealed by a rapid thermal annealing process for 1 min at 400°C as shown in Fig. 6c. When the sample was annealed at

Figure 3. Emission spectra of a Cl₂/CH₄/H₂/Ar discharge with the MQW sample being etched in the reactor at 1000 W of ICP power and 200 W of rf power.

Figure 4. The etch rate of the MQW and the induced dc bias of the MQW and GaN as a function of rf power at 20% of CH₄ and 100 W of ICP power.

Figure 5. SEM micrographs of the surface profile of the MQW etched by Cl₂/H₂/Ar plasma (a) with CH₄ and (b) without 20% of CH₄.
Figure 6. I-V characteristics of a GaN Schottky diode (a) before and (b) after exposure to an ICP Cl₂/CH₄/H₂/Ar plasma (1000 W of ICP power and 100 W of rf power), and after annealing at (c) 400 and (d) 600°C.

600°C, the J-V characteristics in Fig. 6d were fully recovered to that of an as-grown sample. This indicates that the Cl₂/CH₄/H₂/Ar plasma etch process, combined with a postannealing process, is suitable for the fabrication of GaN, InGaN, and GaN/InGaN MQW-based devices.

Conclusions

The dry etching of GaN and In₀.₁₂Ga₀.₈₈N as well as GaN/InGaN MQW has been performed using an inductively coupled Cl₂/CH₄/H₂/Ar plasma at room temperature. The etching characteristics were studied as functions of ICP power and rf power. An optimized concentration of CH₄ in the gas mixture produced the same etch rates for GaN and InGaN. The surface and the sidewall of GaN/InGaN MQW, etched under the same conditions, were also smooth due to the nonselective etch process. This result is very important in the fabrication of laser diodes, since the facets of the laser cavity must have a very smooth surface and a vertical shape. The etch rate of GaN was linearly increased with increasing ICP power, but that of InGaN was saturated above 1000 W of ICP power. With an increase in the rf table power, the etch rate of the MQW also increased in a linear manner. The reverse current in an n-GaN Schottky diode was investigated, in order to evaluate etch-induced damage. The postannealing treatment of GaN surface etched by a Cl₂/CH₄/H₂/Ar plasma was found to be effective in recovering the surface damage.

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