Synergy Effect of Xenon Plasma Ions and Ultraviolet Lights on GaN Etch Surface Damage and Modification

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Surface damage/modification of n-GaN by Xe plasma etching has been investigated for a variety of gas pressures and etching times, using an experiment and a simulation. The result has been compared with that for the Kr plasma etching. The surface morphology etched by the Xe plasma is dependent on gas pressure and etching time. At a low gas pressure (10 mTorr), where there is no UV light emission from the plasma, the surface morphology is observed to be as smooth as that of the as-grown surface, and is independent of etching time. At a high gas pressure (50 mTorr), where there is the UV radiation emission resulting from XeII, there are defects on the etched surface when the etching time increases (200 min), which would probably result from synergy effect of the Xe plasma ions and UV radiations. This result is significantly different from that etched by the Kr plasma which does not change from that of the as-grown surface. The simulation also shows that the Ga/N ratio at the surface etched by the Xe plasma is lower than that by the Kr plasma, which would be related to the difference between the surface morphologies by these two plasmas.

Key words: plasma etching damage/modification, xenon, ultraviolet radiation, n-GaN, preferential etching, synergy effect

1. INTRODUCTION

Gallium nitride (GaN) is an outstanding candidate semiconductor for high power and high temperature microelectronic devices (HEMT and MOS) as well as light-emitting devices (LED) [1,2]. For that reason, GaN has a variety of excellent characteristics: wide band gap energy of 3.4 eV, strong binding energy of 9.12 eV, high breakdown field of 5×10^6 V/cm, and high electron saturation velocity of 2.5×10^7 cm/s [3]. However, unlike Si, there are lots of issues in the GaN-based microelectronic device fabrication processes, because GaN is a binary compound. In particular, preferential etching of a binary compound, which is a nonstoichiometric removal type of plasma-induced surface damage/modification, is a major issue in plasma etching. The preferential etching of GaN causes a change in the composition of its surface such as Ga-rich and N-rich. As a consequence, the surface damage/modification results in degradation of the GaN-based microelectronic device performances such as the leakage current excess from the Schottky contact.

Until nowadays, GaN etch surface damage/modification by capacitively coupled RF Ar and Kr plasmas has been studied by the authors, in order to clearly elucidate the correlation between the discharge plasma behavior and the surface damage/modification properties [4-7]. That study clarified a fascinating result: for the Ar plasma etching, there are many types of

defects or pits on the etched surface, whereas for the Kr plasma etching, there is no defect on the etched surface, which is almost similar to that of the as-grown GaN surface. The occurrence of surface defects by the Ar plasma etching was found to be dependent on the gas pressure and etching time, which probably results from synergy effect of plasma ions and UV radiation emitted. However, the occurrence of surface defects has not been clarified in detail, in particular, if GaN surface defect occurs for other types of processing plasma. Therefore, it is necessary to study this issue for other processing plasmas to improve dramatically the GaN microelectronic device performance.

In this study, n-GaN etch surface damage/modification by Xe plasmas was studied by experiment and simulation, from the viewpoint of synergy effect of plasma ions and UV radiation emitted from the plasma. This result has been compared with that from Kr plasma etching. The comparison is useful for a clear understanding of the Xe plasma etch damage/modification results, because GaN preferential etching properties by the Xe and Kr plasmas are similar according to the simulation described below. Emphasis is placed on changes of GaN etch surface damage/modification properties (the surface morphology and the Ga/N ratio calculated) by the Xe plasma for different gas pressures and etching times.

2. EXPERIMENT AND SIMULATION

For n-GaN Xe plasma etching, a capacitively coupled RF plasma reactor named CPA was employed. This reactor has an asymmetric electrode system with a cathode/anode area ratio of 78 cm²/380 cm². The cathode, on which n-GaN was placed, was connected to a 13.56 MHz RF power supply with a maximum voltage, $V_{RF} = 200$ V. The anode, which is 4 cm away from the cathode, is electrically grounded. The Xe gas pressure was varied from 5 to 10 and 50 mTorr at a constant flow rate of 15 ml/min. For the Xe plasma, the self-bias voltage $|V_{DC}|$ generated on the cathode was almost equal to V_{RF} ($V_{DC} = -200$ V). The V_{DC} for the Xe plasma is the same as that for the Kr plasma. The UV radiation spectra emitted from the Xe plasmas were measured using a spectroscope (Ocean Optics USB2000). For details of the Kr plasma etch experiment, see ref. 7. The specimen used was a 4 μm thick n-GaN film (Si-doped GaN), which was epitaxially deposited on (0001) sapphire substrate by MOCVD (Nichia Corporation). The thin film was rinsed successively in acetone and methanol in an ultrasonic bath for 3 min, in order to remove contamination from its surface. Then it was cleaned by deionized water. After the plasma etching, the surface morphologies of the thin films were observed using SEM (JEOL JSM-6400). The times of plasma etch were 5, 60, 100 and 200 min.

A particle model named PIS developed on the basis of PIC/MCS [8] and BCA/MCS [9] was also employed in the above-described experiment condition. This model consists of two parts, the Xe plasma discharge and the GaN plasma etching. For the Xe plasma discharge, in addition to charged particle movement obeying the Newton and Poisson equations (for details see ref. 8), the elastic, excitation, and ionizing reactions between e^- and Xe are modeled using their reaction cross sections [10]. The elastic and charge exchange reactions between Xe^+ and Xe are also included using the hard sphere model, in the same manner of reactions between Ar^+ and Ar [11]. For the GaN plasma etching, the elastic and inelastic reactions of moving particles (Xe, Ga, N) with target solid particles (Ga, N) and electrons in the solid are modeled based on the same scheme as that used in BCA/MCS. The surface binding energy is assumed to be the GaN binding energy of 9.12 eV. Using the particle model, a change in the self-consistent energy of Xe^+ plasma ions impinging on the cathode with gas pressure is calculated. A change in the Ga/N ratio on the surface by impinging Xe^+ plasma ions with gas pressure and etching time is also calculated. For details of the Kr plasma etch model, see ref. 7.

3. RESULTS AND DISCUSSION

3.1 RF Discharge Plasmas

Figure 1 shows a comparison, obtained by the PIS simulation, in energy and flux between Xe^+ and Kr^+ plasma ions impinging on the cathode (n-GaN). The average energy of the impinging Xe^+ plasma ions decreases with increasing gas pressure. For each chosen gas pressure, the average energy of the impinging Xe^+ plasma ions (solid circles) is almost the same as that of the impinging Kr^+ plasma ions (open circles). The same impinging energy for the Xe and Kr plasmas is due to the same self-bias voltages (V_{DC}), generated on the

cathode in these two plasmas. The impinging ion energy seems to be valid, because the measured etch depth for the Kr plasma was reproduced using the calculated ion energy [7] (for the Xe plasma its etch depths at an etch time of 200 min are much too low to measure it, which indicates that they are less than 50 nm, whereas the calculated etch depths are distributed at 15 to 20 nm). In contrast, the flux of the impinging Xe^+ plasma ions increases with increasing gas pressure, which was obtained from the experimental data, $I_{DC}/(eS_K) \approx (P_{RF}/|V_{DC}|)/(eS_K)$, assuming that the RF current (I_{RF}) leads V_{RF} by a phase of exactly 90°, where I_{DC} is the V_{DC} current, e is the elementary charge, S_K is the cathode area, and P_{RF} is the RF power, respectively. At each gas pressure, the flux of the impinging Xe^+ plasma ions is higher than that of the impinging Kr^+ plasma ions. The higher flux of the impinging Xe^+ plasma ions is consequence of the Xe plasma density generated, which is higher due to the Xe ionization voltage (12.12 eV) lower than that of Kr (13.96 eV).

Fig. 1. Ion energy and ion flux impact dependences on gas pressure for Xe and Kr plasmas.

Figure 2 shows a comparison between the UV radiation spectra emitted from the Xe and Kr plasmas. The UV radiation spectrum emitted from the Xe plasma is dependent on the gas pressure; below 10 mTorr there is no UV radiation spectrum, and as the Xe gas pressure increases to 50 mTorr, the UV radiation spectrum presents a peak at ~350 nm, which is close to the GaN gap energy. The UV radiation spectrum emitted from the Xe plasma results from XeII transition lines (6p-5d and/or 6p-6s) [12]. This indicates the contribution of Xe^+ plasma ions to the emitted UV radiation spectrum; in other words, there is no contribution of excited neutral Xe. For the Kr plasma the same begins to occur at little higher wavelength values, whose peak is distributed at 360 to 380 nm, which has a higher wavelength than that by the Xe plasma. The UV irradiation spectrum emitted from the Kr plasma is due to KrII (5d-5p and/or 6s-5p) transitions, which indicates the contribution of Kr^+ plasma ions [7].

Fig. 2. Spectra of UV radiation emission dependences on Xe and Kr plasma gas pressure.

3.2 Etch Surface Damage and Modification

Figure 3 shows SEM images of n-GaN surfaces etched by the Xe plasma for different gas pressures and etching times. At a low gas pressure (10 mTorr), the surface morphology etched by the Xe plasma is observed to be as smooth as that for the as-grown surface (the results at 5 and 60 min are similar to that for the as-grown) [Fig. 3(a)]. This result does not change even when the etching time lengthens to 200 min [Fig. 3(c)]. The result for the surface morphology etched by the Xe plasma generated at 10 mTorr is the same as that obtained through the Kr plasma etch. The surface morphology etched by the Kr plasma also does not change from that of the as-grown surface with increasing time of the etching [7]. However, according to the PIS simulation, the Ga/N ratio at the GaN surface etched by the Xe plasma is significantly changed with increasing time of the etching. As shown in Fig. 4(a), the Ga/N ratio for the Xe plasma at 10 mTorr decreases to less than 0.5 when the etching time lengthens to 200 min. For the Kr plasma, a similar result is shown in Fig. 4(b): the Ga/N ratio at 10 mTorr decreases with increasing time of the etching, but it is higher than that for the Xe plasma. The reason for the decrease in the Ga/N ratio is that Ga is preferentially etched (or emitted) from GaN by Xe^+ or Kr^+ because the maximum elastic transferable energy of a projectile ion (Xe^+ or Kr^+) to a Ga target atom is higher than that of the ion to a N target atom (Ga atoms in GaN move better due to its higher elastic transferable energy from Xe^+ or Kr^+) based on a simple binary collision model [7,9]. This result indicates formation of Ga vacancies at the surface (or N-rich surface), creating N dangling bonds at deep levels above the valence band that trap both electrons and holes [13,14]. The Ga vacancy formation results in a decrease in the electron concentration in n-GaN, because the Ga vacancies behave as the deep acceptor-like defects [14]. However, if N_2 molecules were formed on and then desorbed from the etched GaN surface, a different result for the Ga/N ratio would be obtained. Namely, if the N_2

desorption occurred together with the preferential etching of Ga, the Ga/N ratio would be close to 1, which may be observed as if the etched GaN surface is the as-grown surface. This is because most N atoms prefer to leave the N-rich surface and to form N_2 molecules, rather than to be incorporated in the N-rich surface due to the high binding energy of N-N [3].

Fig. 3. SEM images of n-GaN surfaces etched by Xe plasmas for different times and pressures.

When the Xe gas pressure increases to 50 mTorr, there is a different result on the etched GaN surface. The surface morphology etched by the Xe plasma at 50 mTorr is dependent on the etching time as shown in Figs. 3(b) and 3(d). At etching times less than 100 min, the surface morphology is observed to be as smooth as that of the as-grown surface [Fig. 3(b)]. When the etching time lengthens to 200 min, there are defects (or point defects) on the etched surface [Fig. 3(d)]. As shown in Fig. 4(a), the Ga/N ratio for the Xe plasma etching at 50 mTorr is decreased with increasing time of the etching in the same manner as that at 10 mTorr, but it is slightly higher than that at 10 mTorr due to the low energy of impinging Xe^+ plasma ions shown in Fig. 1. The calculated result that the Ga/N ratio at 50 mTorr is higher or closer to 1 does not explain the experimental data for the formation of defects: the result calculated by the physical etching effect only indicates that the specimen etched at 50 mTorr is less damaged, whereas the SEM image shows that it is more damaged. In contrast, the surface morphology etched by the Kr plasma is independent of etching time (and gas pressure) as has already been reported in ref. 7: for the Kr plasma etching the surface morphology has no surface defect even when the etching time lengthens to 200 min. For the Kr plasma etching at 50 mTorr, almost similar trends are shown in Fig. 4 (b).

The formation of defects on the surface etched by the Xe plasma seems to be caused by synergy effect of the Xe plasma ions and UV radiation emitted from the plasma [6]. This happens because there is a similarity between the Xe and Ar plasma etching surface damages: the formation condition of surface defect by the Xe plasma etching is almost similar to that by the Ar plasma etching [4]. Namely, for the Xe and Ar plasma etchings, the surface defect tends to be formed at the high gas pressure and long etching time (for 50 mTorr, at more than 100 min or at least 200 min there occurs the

synergy effect). From the viewpoint of the synergy effect, a comparison of the Xe plasma etching result (surface defect) with the Kr plasma etching result (no surface defect) most likely indicates the following two factors relevant to the formation of surface defects induced by the Xe plasma etching. The first factor is that the Ga/N ratio for the Xe plasma etching is lower than that for the Kr plasma etching as shown in Fig. 4, which indicates that a change in the composition of GaN by the impinging Xe^+ plasma ions is more intense. The second factor is that the UV radiation peak wavelength emitted from the Xe plasma at 50 mTorr is shorter than that from the Kr plasma as described above, which means that, for the Xe plasma, the UV photon energy that generates hole-electron pairs in the GaN surface (which is higher than the GaN gap energy) is higher. Due to the higher UV photon energy emitted from the Xe plasma, the Ga-N bonds at the etched surface seem to be much more weakened selectively with increasing time of the etching (or with increasing time of UV irradiation, which corresponds to an increase in the UV light intensity) [15]. As a result, the Ga-N weakened bonds at the surface would be more damaged selectively by the bombarding Xe^+ plasma ions as shown in the SEM image of Fig. 3(d). Therefore, the formation of defects seems to be ascribed to the irradiation of UV light on the surface up to 200 min, whose photo energy is higher than the GaN gap energy: the defect formation would be related closely to the photo energy and UV light intensity (UV light irradiation time). Detailed investigation for the GaN etch surface damage/modification will be necessary in the future.

Fig. 4. Calculated Ga/N ratios at GaN surfaces etched by Xe^+ and Kr^+ impinging plasma ions, as a function of etching time and gas pressure.

4. CONCLUSION

For a variety of gas pressures and etching times, surface damage/modification of n-GaN by the Xe plasma etching has been studied using an experiment and a simulation. The result has been compared with that by the Kr plasma etching. The surface morphology etched by the Xe plasma is dependent on gas pressure

and etching time. At a low gas pressure (10 mTorr), at which there is no UV radiation emission from the plasma, the surface morphology is observed to be as smooth as that of the as-grown surface. This result is not changed even when the etching time lengthens to 200 min. At a high gas pressure (50 mTorr), at which there is the UV radiation emission resulting from XeII , there are defects on the etched surface when the etching time lengthens to 200 min, which would probably result from synergy effect of the Xe plasma ions and UV radiations emitted from the plasma. The result by the Xe plasma etching is significantly different from the Kr plasma etching, which does not change from that of the as-grown surface even when the gas pressure and etching time are increased. The simulation also shows that the Ga/N ratio at the surface etched by the Xe plasma is lower than that by the Kr plasma, which would be related to the difference between the surface morphologies etched by both plasmas.

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