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Dry etching of ZnO films and plasma-induced damage to optical properties

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To study the effects of plasma chemistries on etch characteristics and plasma-induced damage to the optical properties, dry etching of ZnO films has been carried out using inductively coupled plasmas of Cl₂/Ar, Cl₂/H₂/Ar, and CH₄/H₂/Ar. The CH₄/H₂/Ar chemistry showed a faster etch rate and a better surface morphology than the Cl₂-based chemistries. Etched samples in all chemistries showed a substantial decrease in the PL intensity of band-edge luminescence mainly due to the plasma-induced damage. The CH₄/H₂/Ar chemistry showed the least degradation of the optical properties. © 2003 American Vacuum Society. [DOI: 10.1116/1.1563252]

I. INTRODUCTION

In recent years, zinc oxide has attracted much attention because of its remarkable properties such as a large bond strength (cohesive energy of 1.89 eV and melting point of 2248 K), a direct band gap energy (3.3 eV), and a large exciton binding energy (60 meV).^{1–3} The ZnO film has analogous properties to GaN in terms of the band gap energy and crystalline structure. Applications of ZnO include ultraviolet light-emitting diodes, laser diodes, and photodetectors, surface acoustic wave devices for a wireless communication system, and high power electronic devices.^{4–7} In order to fabricate such a device, the ZnO films have to be processed by means of a device processing technology. The fabrication of these ZnO-based optoelectronic devices requires a dry etching technique. Plasma etching has been predominantly used in patterning of GaN-based semiconductors. Recently, the most significant advancement in dry etching of the III nitrides is the utilization of high density plasmas, in which plasma density (or the ion flux) and ion energy are controlled independently. Several research groups reported etch characteristics of the III nitrides,^{8–19} but very little work except by Lee *et al.*²⁰ has been reported on the dry etching of the ZnO films. Furthermore, to our knowledge, no results were reported on the plasma-induced damage of ZnO films. Plasma-induced damage often occurs under conditions of high ion flux and energetic ion bombardment. It includes lattice defects (or dislocations) and formation of dangling bonds on the surface mainly due to energetic ion bombardment, sidewall damage, hydrogen passivation, polymer deposition and etch products deposition, and unequal removal rate of elements.²¹

In this article, we report the effects of plasma chemistries on the etch characteristics of ZnO films and the plasma-

induced damage to optical properties. Dry etching of the ZnO films has been carried out using inductively coupled plasmas of Cl₂/Ar, Cl₂/H₂/Ar, and CH₄/H₂/Ar. Experimental results were discussed in terms of etch rates, surface morphology, and photoluminescence (PL) intensity at room temperature.

II. EXPERIMENT

The ZnO films were grown on *c*-plane sapphire substrates in a horizontal metalorganic vapor phase epitaxy (MOVPE) system using diethylzinc and oxygen. The films grown at 500 °C showed strong UV absorption at 3.22–3.24 eV and a dominant excitonic emission at room temperature. The typical thickness of the films grown for 1 h was about 1 μm. Details are available elsewhere.²²

Etching was performed in a planar-type inductively coupled plasma (ICP) system (Vacuum Science ICP etcher, VSICP-1250A), in which the ICP source operated at 13.56 MHz. The temperature of the backside cooled chuck was held at 25 °C. The ion energy was controlled by the applied radio frequency (rf) chuck power at 13.56 MHz. Unless mentioned, the dry etching of the ZnO films was carried out at 700 W (or 6.6×10⁻² W/cm³) ICP power, 150 W (or 1.9 W/cm²) rf chuck power, 5 mTorr, and total gas flow rate of 25 sccm.

For etch rate experiments, samples were patterned with carbon-paste photoresist, etch depths were obtained from stylus profilometry measurements of etched samples after removal of the photoresist. Surface morphology of etched ZnO films was examined using atomic force microscopy (AFM) operating in tapping mode with Si tip. PL measurements were performed at room temperature using a He–Cd laser (325 nm) as the exciting source. A typical scan range was 2.0–3.5 eV with a resolution of 0.1 nm.

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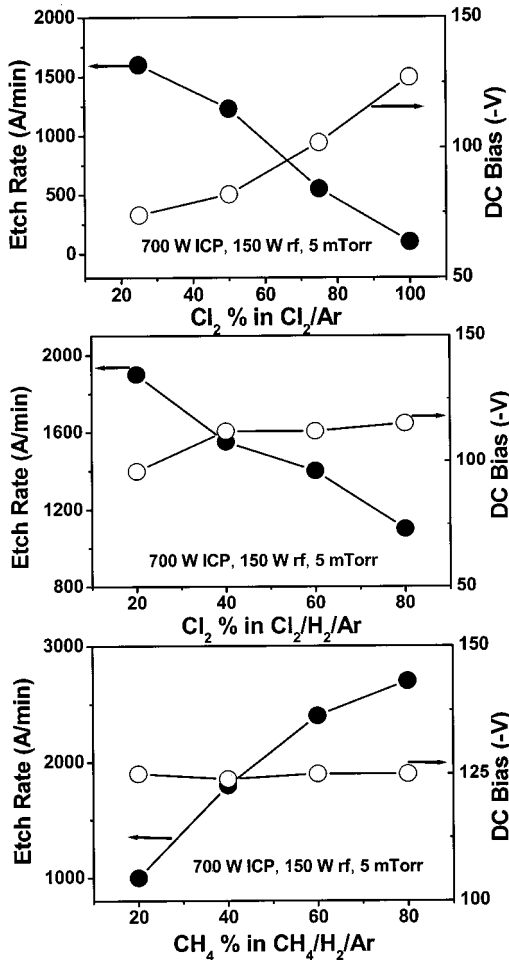


FIG. 1. Effect of plasma chemistries on etch rate of ZnO film and dc bias: Cl₂/Ar (top), Cl₂/H₂/Ar (middle), and CH₄/H₂/Ar (bottom).

III. RESULTS AND DISCUSSION

Figure 1 shows the effects of plasma chemistries on etch rate of ZnO films and dc bias. During these experiments, the ICP source power, the rf chuck power, and the chamber pressure were kept constant at 700 W, 150 W, and 5 mTorr, respectively. Cl₂/Ar, Cl₂/H₂/Ar, and CH₄/H₂/Ar were examined in terms of etch rate. The etch rate decreased with increasing the Cl₂ concentration in Cl₂/Ar (top) and Cl₂/H₂/Ar (middle), but increased substantially with CH₄ percentage in CH₄/H₂/Ar discharges (bottom). These results are attributed mainly to difference in volatilities of the etch products. The Cl₂- and CH₄-based etch gases presumably produce etch products of ZnCl_x and (CH₃)_yZn, respectively. The latter has a higher vapor pressure than the former (for example, 301 Torr at 293 K for (CH₃)₂Zn²³ and 1 Torr at 700 K for ZnCl₂²⁴), which may account for a faster etch rate. The CH₄/H₂/Ar chemistry showed the highest etch rate of 2800 Å/min at 80% CH₄, 700 W ICP, and 150 W rf, which was faster than the one previously reported (2000 Å/min with CH₄/H₂ at 1500 W ICP and 200 W rf chuck power²⁰). Figure 1 also shows that, although the rf chuck power was kept at constant, the dc bias was dependent of the etch gas composition. The increase in the dc bias with Cl₂/Ar and Cl₂/H₂/Ar discharges is probably because additional collisional energy losses are present with increasing Cl₂ concentration, resulting in less production of ions, unlikely in CH₄/H₂/Ar discharges. Although not illustrated, the etch rates of the ZnO films were quite dependent on the ICP source power and the chuck power, that is, increase in etch rate with these variables, typical in the ICP etcher.^{16–19}

Figure 2 shows the AFM images in terms of the effects of the plasma chemistries of Cl₂/H₂/Ar and CH₄/H₂/Ar on surface morphology of the ZnO films etched at 700 W ICP,

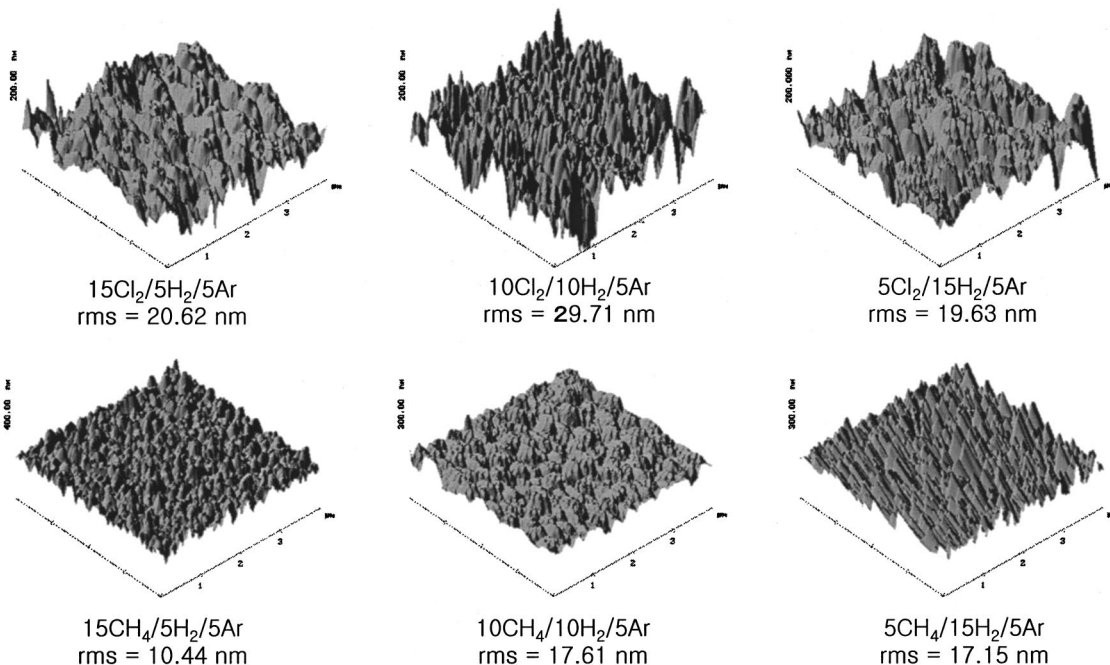


FIG. 2. AFM images of ZnO films etched in Cl₂/H₂/Ar (top) and CH₄/H₂/Ar (bottom).

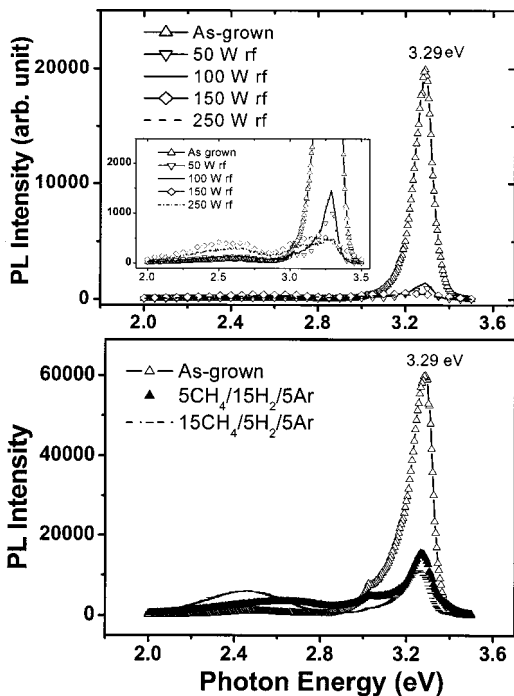


Fig. 3. PL spectra of ZnO films etched in Cl_2/Ar varying rf chuck power (top) and $\text{CH}_4/\text{H}_2/\text{Ar}$ at different H_2 concentrations (bottom).

150 W rf chuck power, and 5 mTorr. The $\text{CH}_4/\text{H}_2/\text{Ar}$ discharges produced a better surface morphology than the $\text{Cl}_2/\text{H}_2/\text{Ar}$, but still rough compared to the roughness of the as grown (rms=15.32 nm). Although not illustrated, the Cl_2/Ar chemistry showed a decrease in rms roughness with Cl_2 concentration (i.e., from 25.3 nm down to 19.4 nm), but much rougher than with the $\text{CH}_4/\text{H}_2/\text{Ar}$ chemistry. Since the ZnO films were grown on *c*-plane sapphire by an MOVPE method without any treatment of the substrate surface, the bad roughness of the as grown is probably due to a high density of defects (mainly threading dislocations) caused by lattice mismatch. It is worth noting that the surface roughness of etched GaN films at moderate etch conditions (700 W ICP, 150 W rf, and 5 mTorr) are 1.1–1.3 nm for GaN films, grown by metalorganic chemical vapor deposition and having rms roughness of about 1.0 nm.^{16,17,19} As a smooth surface is necessary for insured optical and electrical properties of the ZnO films, it is required to further study the optimizing of the ICP etch process as well as developing a growth technique for quality ZnO films in terms of smooth morphology and crystallinity.

Figure 3 shows the room-temperature PL spectra of the ZnO films etched in Cl_2/Ar at 700 W ICP, 50% Cl_2 and 5 mTorr varying the rf chuck power from 50 to 250 W (top), and in $\text{CH}_4/\text{H}_2/\text{Ar}$ at 700 W ICP, 150 W rf, 5 mTorr varying the H_2 concentration (bottom). It is worth noting that the $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasmas showed similar PL spectra to those with Cl_2/Ar . Compared to the strong band-edge luminescence of the as-grown ZnO films at 3.29 eV and no deep-level emission at 2.4–2.6 eV, etched samples in both chemistries showed a substantial decrease in the PL intensity but some-

what of an increase in deep-level emission intensity. The origin of the deep-level emission is believed to be attributed to plasma-induced damage and native defects such as O vacancies and Zn interstitials.^{20,25,26} A more severe degradation was observed with Cl_2 -based chemistries and with more ion energies probably because of surface roughness and plasma-induced surface damage (top). By contrast, the $\text{Cl}_2/\text{H}_2/\text{Ar}$ plasmas showed less degradation of the optical property (bottom). It is also interesting to see that a higher H_2 concentration (or lower CH_4 percentage, represented by solid triangles) resulted in less degradation of the band-edge PL intensity and a decrease in the deep-level emission intensity. Lee *et al.*²⁰ also observed that hydrogen-containing ICP etching enhanced the band-edge luminescence of the ZnO film, grown on a *c*-plane sapphire using an rf magnetron sputtering method and having a very weak band-edge luminescence but a strong deep-level emission. They claimed that the PL enhancement was due to the hydrogen passivation of defects in the ZnO lattice.^{27–29} We also observed somewhat of an enhancement of the band-edge luminescence and a reduction of the deep-level emission with a higher H_2 concentration (Fig. 3, bottom), but no such improvement in the case of $\text{Cl}_2/\text{H}_2/\text{Ar}$ ICP etching. Compared to the ZnO film grown by the rf magnetron sputtering method, which induced a surface damage and thus a weak band edge and strong deep-level emissions,²⁰ the ZnO film prepared by the MOVPE showed a strong band-edge luminescence as shown in Fig. 3, indicating a better quality than the former. The ICP etching of the former with H_2 -based chemistry may improve the surface morphology of the as grown by reactive-ion etching. Hence, in addition to the hydrogen passivation of defects in the ZnO lattice, this may enhance the optical properties of the former. By contrast, the degradation of the band-edge luminescence for the latter could be exaggerated compared to that for the former because of the strong PL intensity of the band-edge emission and a relatively high magnitude of the etch damage. However, it remains controversial and a further study is required to clearly elucidate the emission mechanism of etched ZnO films.

IV. SUMMARY AND CONCLUSIONS

Inductively coupled plasma etching of ZnO films grown by a metalorganic vapor epitaxy method has been carried out to study the effects of plasma chemistries on etch characteristics and plasma-induced damage to the optical properties. Cl_2/Ar , $\text{Cl}_2/\text{H}_2/\text{Ar}$, and $\text{CH}_4/\text{H}_2/\text{Ar}$ were examined at moderate ICP etch conditions (700 W ICP, 150 W rf, and 5 mTorr). The $\text{CH}_4/\text{H}_2/\text{Ar}$ chemistry showed an increase in the etch rate and produced the highest etch rate of 2800 Å/min at 80% CH_4 , which was much faster than the one previously reported. By contrast, the Cl_2 -based chemistries showed a decrease in etch rate with Cl_2 concentration mainly due the involatility of the etch products. The $\text{CH}_4/\text{H}_2/\text{Ar}$ discharges produced a better surface morphology than the $\text{Cl}_2/\text{H}_2/\text{Ar}$, but a quite rougher surface than the roughness of the etched GaN films. Compared to the strong band-edge luminescence of the as-grown ZnO films at 3.29 eV and no

deep-level emission at 2.4–2.6 eV, etched samples in all chemistries showed a substantial decrease in the PL intensity but little increase in deep-level emission intensity. The CH₄/H₂/Ar chemistry showed an enhancement of the band-edge luminescence and a reduction of the deep-level emission at a higher H₂ concentration, but no such an improvement with the Cl₂-based ICPs. Less severe degradation of the ZnO films etched with CH₄/H₂/Ar may be attributed to hydrogen passivation of defects in the ZnO lattice.

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