Dry Etching of ZnO Using an Inductively Coupled Plasma

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In recent years, zinc oxide (ZnO) films have been the subject of considerable interest in terms of their potential application to, for example, surface acoustic wave (SAW) devices in wireless communications, and as a substrate or buffer layer for the growth of GaN-based optoelectronic devices. Recently, an optically pumped laser emission has been observed for the case of ZnO films deposited on sapphire. Along with bandgap tunability from 2.8 to 3.3 eV and 3.3 to 4 eV as a result of alloying with CdO and MgO, respectively, the p-type doping of ZnO has been achieved, using Ga and N codoping, which opens up the possibility of the development of optoelectronic devices from ZnO films. In order to fabricate optoelectronic devices, ZnO films should show high electronic and structural qualities. In addition, it must be easily processed by means of standard device processing technology. However, systematic studies relative to processing technology, such as ohmic contact metallization and etching, have not been forthcoming. Since most epitaxial ZnO films have been grown on sapphire, which is an insulator, it is necessary to etch the ZnO film, in order to provide for ohmic contact, in a manner similar to GaN-based optoelectronic devices.

Several groups have previously reported that ZnO can be etched in acid solutions, including mixtures of HNO3 - HCl - H2O, such as (CH3 )4NNO3. However, a detailed study of the wet etching technique has not yet been reported. In terms of device fabrication, optimization of the etch process is needed in order to achieve a vertical etch profile, a smooth etch surface, and a high etch rate. It is well known that dry etching techniques represent the procedure of choice, since etch requirements are more easily controllable, as mentioned previously, especially for laser facets and mirrors. With such advantages in obtaining reliable pattern transfer, it would therefore be of great interest to investigate the dry etching characteristics of this material.

In this paper, we present the results of a study on the inductively coupled plasma (ICP) etching characteristics of ZnO. The influence of plasma chemistry, self-bias voltage, and ICP power on etch rates are presented. In addition, effects of dry etching on the optical properties of ZnO were studied. Etch profiles and etched-surface morphologies were also investigated.

Experimental

Nominally undoped 1 μm thick ZnO films (n=5 × 1017 cm–3) were epitaxially grown on a c plane sapphire substrate by means of an rf magnetron sputtering method. A detailed description of growth procedures and structural characterizations is provided elsewhere. The ICP reactor, equipped with a 3 kW ICP power supply, was connected to a load-lock chamber. The dc bias for ion energy was provided by superimposing an rf table bias (13.56 MHz) on the sample. All samples were mounted on an anodized Al carrier clamped to a cathode and cooled at the back side with He gas. The base pressure reached a pressure of less than 1 × 10–6 Torr prior to the etching experiments. A carbon-based photoresist was used as an etch mask. All the samples were loaded into the ICP process chamber through the load lock. The etch conditions used in this study were 10 mTorr chamber pressure, 500–2500 W of ICP power, 20°C table temperature, and 0–200 W rf power. During the etching process, the plasma was monitored by optical emission spectroscopy. Etch rates were measured with a surface profilometer after the photoresist (PR) mask was removed. Etch anisotropy and etched surface morphology were examined by scanning electron microscope (SEM) and atomic force microscope (AFM). Photoluminescence (PL) measurement using a He-Cd laser as the excitation source (λ = 325 nm) was used to investigate the optical property of etched films.

Results and Discussion

Table I summarizes the etch rates for ZnO, which were obtained by employing various plasma chemistries. The highest etch rate was obtained for a sample which had been etched using CH4/H2 chemistry. In this case, an optical emission spectral line of CH radicals at 431.4 nm, which is one of the CH fragments formed in the CH4 plasma, indicative of the presence of active CH radicals in the plasma (not shown). This suggests that the surface reaction of ZnO with CH radicals is favorable, thus resulting in a volatile metalorganic zinc compound, such as (CH3 )2Zn as an etch product. The compound (CH3 )2Zn, for example, has a very high vapor pressure of 301 Torr at 20°C, resulting in the highest etch rate, but the vapor pressures are only 1 Torr for ZnCl2 and ZnF2, at temperatures as high as 428 and 124°C, respectively. Table I shows that the etch rate of ZnO by the CH4/H2 chemistry are very high and that the etch rate increases with an increase in the total flow rate of the CH4/H2 gas mixture but the etch rates are drastically decreased by chlorine and fluorine chemistries.

To investigate the effect of ion energy on the etch characteristics of ZnO, the etch rates were monitored at different rf table powers. Figure 1 shows the etch rate of ZnO as a function of rf table power using CH4/H2/Ar (30/8/16 sccm) plasma conditions at an ICP power of 1500 W. The ICP power was varied from 0 to 2500 W. Figure 2 shows the etch rate of ZnO as a function of self-bias voltage using CH4/H2/Ar (30/8/16 sccm) plasma conditions at an ICP power of 1500 W. The self-bias voltage was varied from 100 to 2500 V. The results show that the etch rate increases with increasing ICP power and self-bias voltage.

Table I. Etch rate at various plasma chemistries under conditions of 1500 W ICP power and 100 W rf table power.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Gas flow rate (sccm)</th>
<th>Etch rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH4/H2</td>
<td>50/25</td>
<td>200</td>
</tr>
<tr>
<td>CHF3/H2</td>
<td>50/25</td>
<td>190</td>
</tr>
<tr>
<td>CF3H2</td>
<td>50/25</td>
<td>245</td>
</tr>
<tr>
<td>CH3H2</td>
<td>30/15</td>
<td>988</td>
</tr>
<tr>
<td>CH4H2</td>
<td>50/25</td>
<td>1200</td>
</tr>
</tbody>
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1500 W. Ar was added in order to stabilize the plasma. When the rf power was increased from 0 to 200 W, the induced self-bias voltage was increased from 0 to −80 V. Therefore, etch rates can be increased as the result of the assistance of bombardment of energetic ions, thus achieving a maximum etch rate of 2000 Å/min. It is noteworthy that the etch rate at zero bias was not zero but about 250 Å/min, indicating that even in the absence of a dc bias, spontaneous etching could be achieved by CH radicals. From this result, we propose that the etch mechanism under this etching condition does not necessarily involve an enhanced physical spattering but, rather, an ion-enhanced mechanism, because even without the ion bombardment the etching of ZnO occurred under purely chemical etching conditions and the strong dependency of etch rate on dc bias in Fig. 1 indicates that the etching of ZnO was enhanced by the ion bombardment.

Figure 2 shows the etch rate as a function of ICP power. Etching was performed for ICP power ranging from 500 to 2500 W at an rf table power of 150 W. Although the rf power was held at 150 W, the induced dc bias was decreased from −190 to −15 V with increasing ICP power because of the higher plasma density which suppresses the cathode dc bias at a higher ICP power. The etch rate, which is normally affected by the density of the reactive ions and neutrals in the plasma, in turn increased due to the increased rate of chemical reactions on the etched surface. This result also supports the previous result that even without ion bombardment, the spontaneous etching could be driven by the chemical components in the etching plasma. It is also noteworthy that the etch rates linearly increased without a maximum in both Fig. 1 and 2, suggesting that only one etch mechanism is operative for all experimental conditions.15

In the fabrication of optoelectronic devices, a vertical etch profile and a smooth etched surface, as well as the etch rate, are also of interest, since it would be expected that a smooth surface would enhance the optical and electrical properties of thin films, thus improving the quality and reliability of the device.16 Figure 3 is a SEM of a ZnO sample etched at an rf power of 150 W (dc bias: −40 V) and an ICP power of 1500 W. The etch profiles of the vertical sidewalls were observed to be highly anisotropic for a wide range of etching conditions. However, some grooves, which might have originated from irregularities in the mask material, were formed on the sidewall, as shown in Fig. 3. AFM and SEMs showed that the etched surfaces were smooth and no residues or pits were produced on the surface.

To understand the effect of dry etching on the optical properties of etched ZnO films, a PL measurement was performed at room temperature. Figure 4 shows the PL spectra of etched ZnO films under a variety of experimental conditions. All samples show band-edge luminescence at 378 nm (3.28 eV) and an enhanced physical sputtering but, rather, an ion-enhanced mechanism under this etching condition does not necessarily involve an enhanced luminescence by a factor of eight and a decrease in the deep-level emission at about 580 nm. However, Saotome et al.18 reported that the dry etching of GaN reduced the band-edge PL intensity by a factor of approximately five, but that a subsequent wet etching of the dry etched GaN sample restored the PL intensity to about half of the original value. We performed a post-experiment on the dry etched ZnO film using a concentrated HF solution, in order to examine the penetration depth of hydrogen passivation in the ZnO film. If the origin of the enhanced luminescence is the ion-damaged surface, the intensity would be reduced to the original value. Figures 4a and d show that the intensity of an as-grown sample is not affected by HF treatment which etches the film to a depth of ca. 200 Å. On the other hand the PL intensities of dry-etched sample were decreased after the wet etching process as shown in Fig. 4b and e, and Fig. 4c and f. However, the PL intensity of the dry-etched sample is still 500 times higher than that of the as-grown sample, even after the wet etching process.

To clarify the origin of the enhanced PL intensity, we performed a H plasma treatment on the ZnO surface and recorded the PL spectra, as presented in Fig. 5. The band-edge PL intensity (I) drastically
We report herein an investigation of the dry etching characteristics of ZnO for the first time in an ICP system. CH$_4$-based chemistry, rather than chlorine and fluorine chemistry, showed the highest etch rate for ZnO, suggesting that the Zn is etched away via the formation of a metallicorganic zinc compound which is highly volatile. An etch rate as high as 2000 Å/min was achieved at an rf power of 200 W under ion-enhanced etching conditions. As the ICP power is increased, the etch rate also increased, indicating that the plasma density is also an important factor in the etching of ZnO. Furthermore, an enhancement in PL intensity was observed on the ZnO film which had been etched with CH$_4$/H$_2$/Ar plasma, and this was attributed to the passivation of defects in ZnO by hydrogen within the depth of 250 Å from the film surface.

Conclusions

We report herein an investigation of the dry etching characteristics of ZnO of the first time in an ICP system. CH$_4$-based chemistry, rather than chlorine and fluorine chemistry, showed the highest etch rate for ZnO, suggesting that the Zn is etched away via the formation of a metallicorganic zinc compound which is highly volatile. An etch rate as high as 2000 Å/min was achieved at an rf power of 200 W under ion-enhanced etching conditions. As the ICP power is increased, the etch rate also increased, indicating that the plasma density is also an important factor in the etching of ZnO. Furthermore, an enhancement in PL intensity was observed on the ZnO film which had been etched with CH$_4$/H$_2$/Ar plasma, and this was attributed to the passivation of defects in ZnO by hydrogen within the depth of 250 Å from the film surface.

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