Jpn. J. Appl. Phys. Vol. 42 (2003) pp. L 535–L 537
Part 2, No. 5B, 15 May 2003

High-Rate Dry Etching of ZnO in $BCl_3/CH_4/H_2$ Plasmas

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(Received December 9, 2002; accepted for publication March 24, 2003)

High-rate dry etching characteristics of aluminum-doped zinc oxide (AZO) have been investigated in inductively coupled plasma (ICP) using $BCl_3/CH_4/H_2$ plasma chemistry. Etch rates were measured as a function of BCl_3 flow rate in $BCl_3/CH_4/H_2$ mixture and dc-bias voltage. Measurement of etch rate, and etched sidewall profile were performed using a stylus profilometer and scanning electron microscopy, respectively. The highest AZO etch rate about 310 nm/min, could be obtained near 80% BCl_3 and at dc-bias voltage of −350 V. [DOI: 10.1143/JJAP.42.L535]

KEYWORDS: AZO, BCl_3, inductively coupled plasma, bias voltage, etch profile

ZnO-related oxide semiconductors are technologically important because of their use in new-generation optoelectronic devices having a wide direct band gap ($E_g = 3.37$ eV) and a large exciton binding energy of 60 meV which is much higher than that of GaN (25 meV).[1,2] To realize ZnO-based optoelectronic devices, it is imperative to develop a ZnO dry etching process with a high etch rate, a high selectivity over mask materials, a highly anisotropic etching profile, and smooth sidewalls.[3,4] For example, to investigate ohmic characteristics of ZnO using a transmission line method (TLM),[5] the formation of ZnO mesa structures by dry etching is required. However, systematic studies on ZnO etching processes have not been extensively carried out. Lee *et al.*[6] reported on the etching characteristics of ZnO in a CH_4/H_2-based plasma. They showed that the highest etch rate about 200 nm/min could be obtained using a gas combination of $CH_4/H_2/Ar$. A study on the inductively coupled plasma (ICP) etching of ZnO in $BCl_3/Cl_2/Ar$ plasma chemistry by one of our groups suggested that the etching mechanism is the formation of a zinc chloride, $ZnCl_X$, while the oxygen in ZnO is removed by the formation of boron oxide.[7] However, more detailed studies on the BCl_3-based plasma etching of ZnO are required to understand the etching mechanism in BCl_3-based plasmas. In this work, we report the ICP etching behavior of n-ZnO epitaxial layers in $BCl_3/CH_4/H_2$ chemistry.

The specimen was Al-doped n-type zinc oxide(AZO) epitaxial layers grown on (0001) sapphire. Before the etching, AZO samples were patterned using a 1.6-μm-thick photoresist and a 0.35-μm-thick chromium (Cr) mask. To etch AZO, a magnetized ICP etcher which has a permanent magnetic bucket inside the chamber and Helmholtz-type axial electromagnets around the chamber wall was used. The details of the magnet configurations used in this experiment and the plasma characteristics can be found elsewhere.[8] The AZO was dry etched as a function of BCl_3 percentage in CH_4/H_2 (3:1) and at dc-bias voltages from −250 V to −350 V, while the ICP power, the working pressure, the total flow rate, and the substrate temperatures were fixed at 1200 W, 5 mTorr, 50 sccm, and 20°C, respectively. The etch rates of AZO and the etch selectivity over photoresist (PR) were estimated from the depth of the etched features measured by a stylus profilometer before and after removing the PR. The profiles of the etched AZO using PR and Cr metal as the etch masks were evaluated with a scanning electron microscope (SEM).

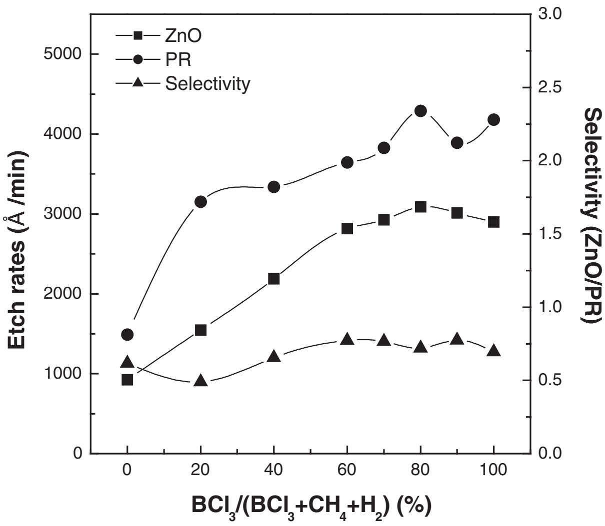

Fig. 1. Etch rate and selectivity over PR as a function of BCl_3 percentage in the $BCl_3/CH_4/H_2$ gas mixture ($CH_3/H_2 = 3:1$) at rf power of 1200 W, working pressure of 5 mTorr, and bias voltage of −350 V.

Figure 1 shows the etch rates of AZO as a function of BCl_3 percentage in $BCl_3/CH_4/H_2$ gas mixtures. The ratio of $CH_4:H_2$ was maintained at 3:1. The dc-bias voltage was maintained at −350 V.

As shown in the figure, the AZO etch rate remarkably increased with the increase of BCl_3 percentage up to 80% but the further increase of BCl_3 percentage in the $BCl_3/CH_4/H_2$ gas mixture decreased the etch rate slightly. It is well known that the formation of a zinc compound, such as $Zn(CH_3)_Y$ in the CH_4-based plasma is the main etching mechanism of Zn in ZnO. In this $BCl_3/CH_4/H_2$ chemistry, as the BCl_3 percentage is increased, the etch rate of zinc oxide is increased until the BCl_3 percentage reaches 80%. The increase of BCl_3 percentage in the $BCl_3/CH_4/H_2$ chemistry decreases both CH_4 and H_2 percentages in the gas mixture. Therefore, it should be noted that BCl_3 in the $BCl_3/CH_4/H_2$ chemistry plays an important role in the etching of ZnO by forming boron, BCl_X, and chlorine ions or radicals in the plasma. Boron and boron chloride ions or radicals help to dissociate ZnO by forming volatile boron–oxygen–chlorine

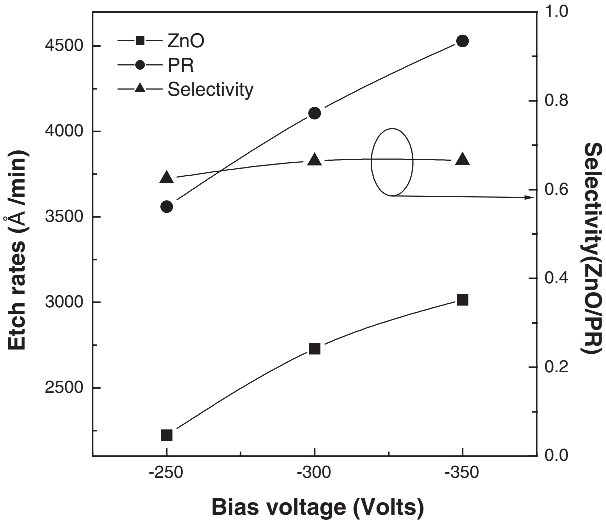

Fig. 2. Etch rate and selectivity over PR as a function of bias voltage for 80% BCl_3 in the $BCl_3/CH_4/H_2$ gas mixture ($CH_3/H_2 = 3:1$), at rf power of 1200 W, working pressure of 5 mTorr, and substrate temperature of 20°C.

compounds such as trichloro-boroxin $(BOCl)_3$, boron oxychloride (BOCl), and boron dioxide (BO_2), whose formation energies are −370, −76, and −59 kcal/mol, respectively.[7] Also, chlorine ions or radicals can increase the etch rate of ZnO by forming volatile $ZnCl_X$ compounds. In addition, a fairly high etch rate of zinc oxide, 290 nm/min, in 100% BCl_3 indicates that the formation of volatile $ZnCl_X$ compound is one of the important etching mechanisms in the etching of ZnO in addition to the formation of $Zn(CH_3)_y$ by CH_4/H_2 in the $BCl_3/CH_4/H_2$ chemistry.

Figure 2 shows the etch rate of AZO as a function of bias voltage applied to the substrate in the $BCl_3/CH_4/H_2$ (80%/15%/5%) gas mixture at rf power of 1200 W, working pressure of 5 mTorr, total gas flow rate of 50 sccm, and substrate temperature of 20°C. As shown in the figure, the etch rates of AZO increased with the increase of dc-bias voltage. Also, the highest etch rate of about 310 nm/min could be obtained at dc-bias voltage of −350 V. In the case of the etch selectivity over PR, it was maintained between 0.62 and 0.67. The increase of both ZnO and PR etch rates with the increase of dc-bias voltage reflects the increase of sputtering effect for both ZnO and PR.

Figure 2(a) and 3(b) show the SEM micrographs of the sidewall profiles of AZO etched in 100% BCl_3 plasma using PR and Cr masks, respectively. Both samples were etched to a depth of 1 μm. In the case of the PR mask, we could not obtain a vertical sidewall profile due to the erosion and sidewall deposition of the PR. On the other hand, the profile etched with the Cr mask shows a fairly vertical etch profile. It can be ascribed to the very high etch selectivity of AZO over the Cr mask. Important factors that affect the verticality of the etched profile can be summarized into several factors such as the thickness, erosion, and sidewall deposition of mask materials. Under our experimental conditions, the PR was as thick as we could use, therefore, we were not able to improve the etch profile further. Also, the sidewall erosion of PR and its redeposition to on the etched sidewall is one possible reason for the degradation of the etched profile. We could observe this possibility in the SEM images and selectivity of AZO over PR and Cr. As shown in Fig. 3, PR was eroded away during etching and was redeposited on the sidewall of AZO. However, in the case of AZO etching with the Cr mask, because there was no erosion of the Cr mask, vertical etch profiles could be obtained (the selectivities of AZO over PR and Cr were about 0.65 and as high as 30, respectively). It is noteworthy that Cr is one of the most useful mask materials for AZO etching.

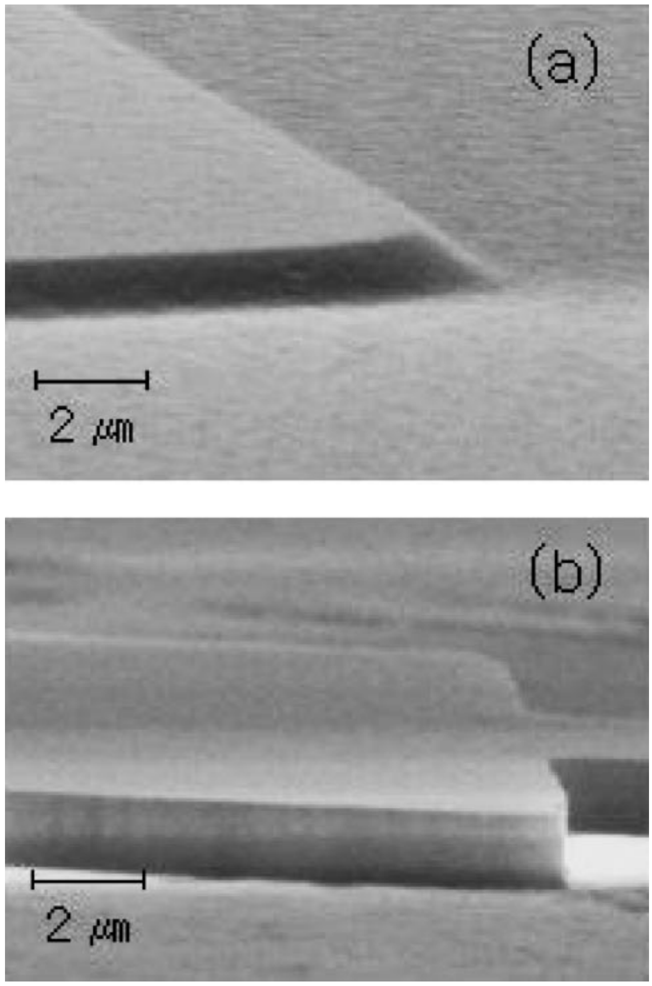

Fig. 3. SEM micrographs of AZO sidewall profiles etched with PR (a) and Cr masks (b) in 100% BCl_3 plasma, at rf power of 900 W, working pressure of 5 mTorr, bias voltage of −350 V, and substrate temperature of 20°C.

In summary, dry etching characteristics of AZO were investigated in magnetized inductively coupled plasma using $BCl_3/CH_4/H_2$ plasma chemistry at room temperature. High etch rates of AZO were obtained possibly due to the formation of volatile compounds such as $Zn(CH_3)_y$ and $ZnCl_x$. Also, the increase of bias voltage helped increase the etch rate of AZO by increasing the sputtering. In order to obtain good sidewall verticality, Cr metal should be used as an etch mask. High selectivity of AZO over Cr mask means that no erosion of Cr mask occurred, which could transfer patterns into AZO layers with the same dimension. An AZO profile etched with a Cr mask in 100% BCl_3 plasma at room temperature shows a fully vertical sidewall profile.

This work was supported by the Post-doctoral Fellowship Program of Korea Science & Engineering Foundation (KOSEF).

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