유도결합 플라즈마를 이용한 ZnO 박막의 식각 특성

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Etch characteristics of ZnO thin films using an inductively coupled plasma

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Abstract : The etching characteristics of Zinc Oxide (ZnO) and etch selectivity of ZnO to SiO_2 in BCl_3/Ar plasma were investigated. It was found that ZnO etch rate shows a non-monotonic behavior with increasing both Ar fraction in BCl_3 plasma, RF power, and gas pressure. The maximum ZnO etch rate of 50.3 nm/min was obtained for BCl_3 (80%) / Ar(20%) gas mixture. The plasmas were characterized using optical emission spectroscopy (OES) analysis measurements while chemical state of etched surfaces was investigated with X-ray photoelectron spectroscopy (XPS). From these data, the suggestions on the ZnO etch mechanism were made.

Key Words : Etch, ZnO, ICP

1. Introduction

ZnO is a wide bandgap energy of 3.37 eV, it is transparent in visible light and it can operate from UV to blue wavelengths. The exciton binding energy for ZnO (~ 60 meV) is higher than that for GaN (~25 meV). A higher exciton binding energy translates to an enhanced efficiency of luminescence. ZnO also exhibits better (compared to GaN) radiation resistance which is important for devices used in space and nuclear applications [1]. However, there are very few reports detailing the dry etching of ZnO using high density plasma sources favored in modern micro-electronic technology. As a result, the influence of process parameters on the ZnO etch rate has not been explored in detail, and the ZnO etch mechanism is still unclear. In this work, we investigated etching characteristics of ZnO thin films using BCl_3/Ar mixtures in an inductively coupled plasma (ICP) system. The plasmas were characterized using OES analysis. The chemical reaction on the surface of the etched ZnO thin film was investigated with XPS.

2. Experimental Details

ZnO thin films were prepared on Si(100) substrate by using sol-gel method. The final thickness of ZnO films is about 160 nm. The etching experiments were performed in an ICP system. The ZnO thin films were etched in BCl_3/Ar plasmas with the variable process parameters were gas mixing ratio, process pressure (1 - 3 Pa), RF power (500 - 900 W). In all experiments, gas flow rate and DC-bias voltage were fixed at 20 sccm, -150 V. Etch rates were measured by using an a-step surface profiler. Changes to the chemical composition in the chamber were analyzed with an OES. Installation of the diagnostic tools was provided through the vertical view port on the chamber's wall-side. The chemical reaction on the surface of the etched ZnO thin film was investigated with XPS.

3. Results and Discussion

Figure 1 represents ZnO etch rate and selectivity of ZnO to SiO_2 as a function of BCl_3/Ar mixing ratio at process pressure of 2 Pa and RF Power of 700 W. It can be seen that ZnO etch rate also increases, but then reaches a maximum of 50.3 nm/min at BCl_3(80%) / Ar (20%). This fact allows one to assume that, for a given range of experimental condition, chemical etch pathway is more effective than physical one. In our opinion, a domination of chemical etch pathway may be explained by two reasons. The first of the melting point for $ZnCl_2$ is about 290 °C, so that it can not be related to hardly volatile compounds. The second of the strength of Zn-Cl chemical bond (229 kJ/mol) is higher than one for Zn-O (159 kJ/mol). Therefore, Cl atoms formed in plasma can react with ZnO spontaneously and no ion bombardment is needed to support chemical reaction by breaking oxide bonds. It was shown that variation of gas mixing ratio causes monotonic changes of electron density, electron temperature, total ion density and Cl atom density [2].

Figure 2 shows the etch rate of ZnO as a function of RF power and process pressure for BCl_3(80%)/Ar(20%) plasma. As RF power increases, the ZnO etch rate also increases, but then reaches a maximum of 50.3 nm/min at 700 W. It can be seen that an increase in RF power causes a monotonic increase in both dissociation and ionization rates and thus, in densities and fluxes of Cl atoms and positive

ions. As for the effect of gas pressure, in our opinion the situation looks as follows. An increase in gas pressure increases the density of neutral chemically active species, but lowers ion mean free path and ion energy.

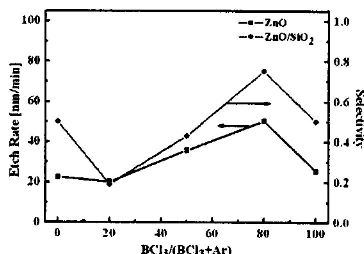

Fig. 1. Etch rate and selectivity of ZnO thin films as a function of BCl_3/Ar gas mixing ratio.

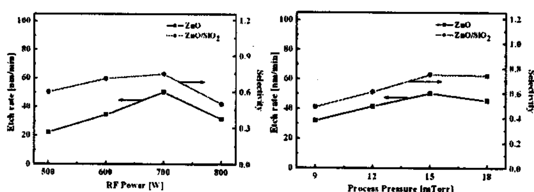

Fig. 2. Etch rate of ZnO thin films as a function of RF power and Process Pressure.

To understand the roles of physical and chemical effects, For these purposes we used the OES analysis. As shown in Fig. 3, the difference between maximum intensity and the intensity in pure BCl_3 plasma is small and quite close to the experimental error. However, even if such maximum do exist, the non-monotonic behavior of BCl density cannot be accepted as an explanation for a non-monotonic etch rate. In BCl_3 plasma, chemical etch pathway dominates over its physical counterpart, so the contribution of physical sputtering by BCl ions seems to be insufficient [3].

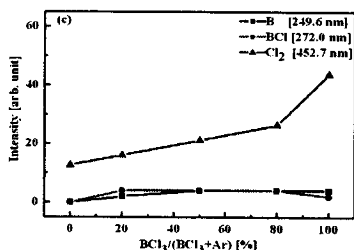

Fig. 3. Emission intensity of ion density as a function of gas mixing ratio.

Figure 4 shows that the Zn 2p and O 1s spectra were at a binding energy of 1021.8 eV and 531.0 eV respectively, suggesting that Zn remained fully oxidized after etching. As shown in Fig. 4(a), this change in chemical shift indicates a chemical reaction between Zn and Cl resulting in the formation of Zn-Cl bonds on the surface. The observed XPS signal originates from the unmodified ZnO subsurfaces as well as the ZnO surfaces modified by the plasma. However, the chemical shift observed in the Zn 2p spectra might suggest that the ZnO layer. Fig. 4. (b) show that the intensities of the first (531.2eV) and second (532.3eV) peaks were reversed for the data obtained from the as-deposited and etched samples. That is, the shoulder peak indicated as O-H from the as-deposited sample is related to the formation of Zn-OH bonds decreased significantly as a result of the preferential removal of the Zn atoms. With the addition of BCl_3 gas, the Zn-O peak intensity became negligible, which demonstrates a dramatic increased chlorination of the etched surface. The intensities of the O-H peaks increased presumably due to the increased formation of $Zn(OH)_2$ in the air. There is also the possibility of O-Cl bond formation even though that was not demonstrated here.

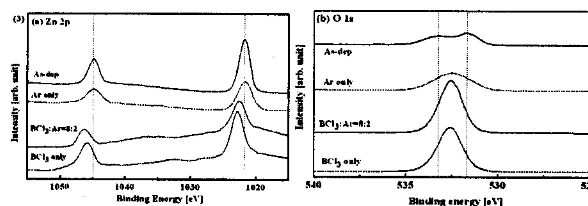

Fig. 4. Zn 2p and O 1s XPS narrow scan spectra of ZnO surfaces etched with gas mixing ratio.

4. Conclusion

In this work, we carried out experimental investigations of ZnO etching mechanism in BCl_3/Ar plasma. We have found that an increase of the BCl_3 content in BCl_3/Ar plasma leads to an increase in ZnO etch rate, which reaches a maximum value of 50.3 nm/min at 80% BCl_3 because a big addition of BCl_3 to the BCl_3/Ar plasma increased the physical effect. Due to the relatively high volatility of by-products formed during the etching by BCl_3/Ar plasma, ion bombardment in addition to physical sputtering was required to obtain high ZnO etch rates. It was found that the reason for etch rate maximum is the concurrence of physical and chemical pathways in ion-assisted physical reaction. It was suggested that volatile oxygen compound such as the XPS result showed that the composition of the etched sampled in the BCl_3 plasma is identical to that of the as-deposited sample. These tendency was very similar to the etch characteristics. This result agreed with the universal energy dependency of ion enhanced chemical etching yields.

Reference

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