Etching Properties of ZnS:Mn Thin Films in an Inductively Coupled Plasma

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ZnS is an attractive material for future optical and electrical devices since it has a direct and wide band gap to provide blue emission at room temperature. In this study, inductively coupled BCl_3/Ar plasma was used to etch ZnS:Mn thin films. The maximum etch rate of 164.2 nm/min for ZnS:Mn was obtained at a BCl_3(20)/Ar(80) gas mixing ratio, an rf power of 700 W, a dc bias voltage of -200 V, a total gas flow of 20 sccm, and a chamber pressure of 1 Pa. The etch behaviors of ZnS:Mn thin films under various plasma parameters showed that the ZnS:Mn were effectively removed by the chemically assisted physical etching mechanism. The surface reaction of the ZnS:Mn thin films was investigated by X-ray photoelectron spectroscopy. The XPS analysis revealed that Mn had detected on the surface ZnS:Mn etched in BCl_3/Ar plasma.

Keywords : Zinc sulfide, Etching, Electroluminescence device, Inductively coupled plasma

1. INTRODUCTION

Zinc sulfide (ZnS) is a wide band gap material to provide blue rays at room temperature. The ZnS thin film has successfully utilized in optoelectric device applications, such as optical coatings, gate dielectrics, filters, and reflectors[1]. Especially, Mn- or Tb-doped ZnS thin films have been widely employed as electroluminescent (EL) phosphor for the application of thin film electroluminescent (TFEL) devices because they offer high brightness and wide viewing angle. The TFEL is composed of bottom electrode, lower insulator, phosphor, upper insulator, and top electrode. The total thickness of TFEL device is as thin as a few micrometers. The simplicity of structure and the thickness of TFEL provide a great potential to be a very high-resolution flat panel display. Especially, in order to overcome crosstalk problem for the color TFEL display devices, it is essential to selectively etch the phosphor layer against the under-layer such as lower insulating layer or etch barrier layer. Therefore, it is very important to develop the micro-patterning process using plasma etch technology.

CH_4/H_2 chemistries had been used to etch ZnS with high dc-self biases and resulted in low etch rate of under 30 nm[1-5]. It reported that the use of CH_4/H_2 gas mixture results in the formation of hydrocarbon polymer, plasma induced damage and a poor reproducibility of the etch process. Inductively coupled plasma (ICP) has some advantages such as high ion density and high etch rate compared to the reactive ion etching (RIE) and could overcome the problems of photo-resist burning or swelling in ECR plasma.

In this work, ZnS:Mn thin films were etched in BCl_3/Ar plasma with using ICP etch system. The etch characteristics of ZnS:Mn thin films systematically investigated with various gas mixing ratio, source RF power, dc bias voltage, and working pressure. The surface states of etched ZnS:Mn thin film was examined with using X-ray photoelectron spectroscopy (XPS).

2. EXPERIMENTAL

The Mn-doped ZnS:Mn (0.39 wt.%) thin films were prepared with using RF magnetron sputtering method. The etching experiments of ZnS:Mn were performed in ICP etch system[6]. The standard conditions were a working pressure of 1 Pa, an RF power of 700 W and DC bias voltage of -200 V. The total flow rate of 20 sccm for BCl_3/Ar gas mixing ratio was fed through a mass flow controller. We discussed the effect of BCl_3/Ar gas mixing ratio in the etch of ZnS:Mn. The behaviors of etch rates were also discussed with RF source power, DC bias voltage and working pressure. The etch rates were obtained from surface-profiler (alpha-Step 500, KLA Tencor) after etching ZnS:Mn for 1 min and removal of the patterned photoresist (AZ1512). The chemical reactions between BCl_3/Ar plasma and ZnS:Mn thin film was investigated with using an XPS (ESCALAB 200R. VG Scientific) with Mg K_α(1253.6 eV) radiation at 300 W. The surface composition and the chemical binding states of the constituents were analyzed with an XPS narrow scan spectra with 20 eV passing energy.

3. RESULTS AND DISCUSSION

The etch result is affected by both chemical and physical mechanisms when the binary mixture of the chemically-active gas with a noble gas is used for the etching process;

(1) The chemical "channel" is controlled by the fluxes of neutral chemically active species on the etched surface.

(2) The physical factor is represented by sputter etching as well as by the activation of chemical reaction through the ion-stimulated desorption of the reaction products.

In such a system, the gas mixing ratio gives a powerful factor to adjust the process results as well as determines the regions where the result is sensitive to the different input parameters. Therefore, the investigation of the etching mechanism requires the simultaneous analysis of the influence of input process parameters on the etch rate behavior and surface kinetics.

Figure 1 shows the etch rates of ZnS:Mn thin film and SiO_2 as a function of BCl_3/Ar plasma gas mixing ratio when total flow rate was maintained at 20 sccm. The RF power to the source, the DC bias voltage, the working pressure, and the substrate temperature were also maintained at 700 W, -200 V, 1 Pa, and 23 °C, respectively. As the BCl_3 addition in $BCl_3/(BCl_3+Ar)$ plasma increases from 0 % to 20 %, the etch rates of ZnS:Mn thin film increases from 134.7 nm/min to 164.2 nm/min. The etch rate of the ZnS:Mn reached the maximum value at 20 % BCl_3/Ar gas concentration and decreased from 161.1 nm to 114.1 nm with further addition of BCl_3 addition (from 50 % to 100 %) in $BCl_3/(BCl_3+Ar)$ plasma. The etch rate of SiO_2 increased from 21.6 nm/min to 156.2 nm/min as the BCl_3 addition in $BCl_3/(BCl_3+Ar)$ plasma increases from 0 % to 50 %. With further addition over 50 % of the BCl_3 addition in BCl_3/Ar, the etch rate of SiO_2 shows a little decrease tendency, but maintains some constant.

Comparison of the ZnS:Mn etch rates in pure Ar and pure BCl_3 plasmas shows that the chemical etching is less effective than physical sputtering. Non-monotonic behavior of the etch rate in our experiments may be explained as follows; It is well known that some of the components for ZnS:Mn form low-volatile chlorides

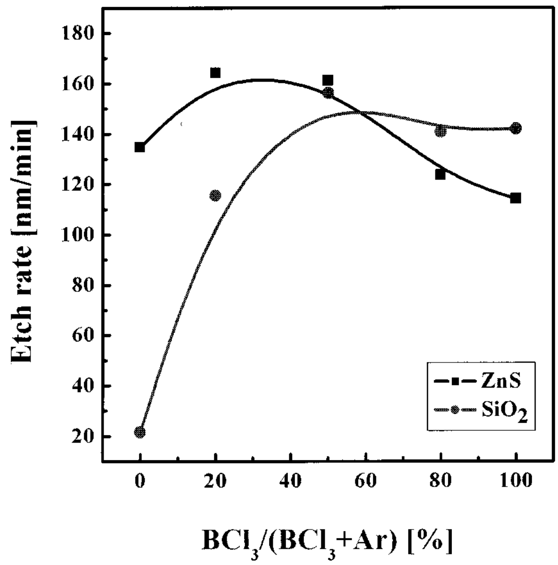

Fig. 1. Etch rate of ZnS:Mn and SiO_2 as a function of $BCl_3/(BCl_3+Ar)$ gas mixing ratio.

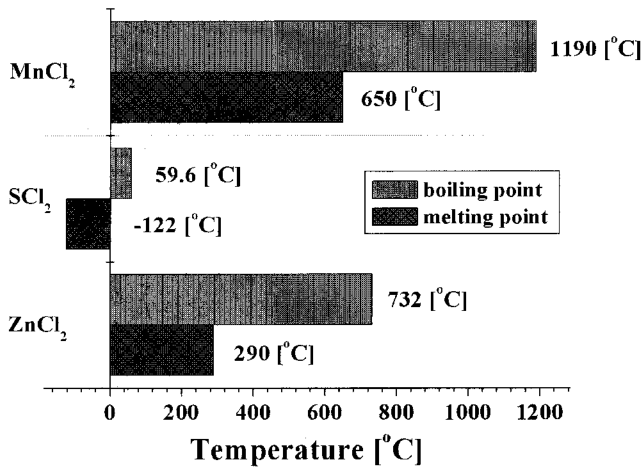

Fig. 2. Melting point and boiling point of ZnS:Mn etching byproducts.

such as $MnCl_2$ (melting point(MP)=650 °C)and $ZnCl_2$ (MP=290 °C), as shown Fig. 2. Among them, $MnCl_2$ is extremely low volatile compound. This fact supposes a negligible role of thermal desorption for Mn-Cl bonds and allows one to assume preliminary the ZnS:MN etch mechanism as ion assisted process where the role of ion bombardment includes such effects as: 1) sputtering of main material; and 2) sputtering (ion stimulated desorption) of reaction products to provide the access of Cl atoms to the etched surface.

Figure 3 shows the effect of RF power on the etch rates of ZnS:Mn and SiO_2 at a $BCl_3/(BCl_3+Ar)$ of 20 %.

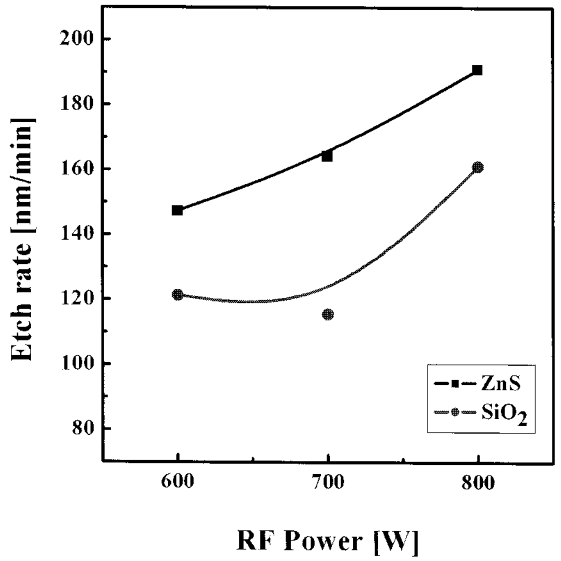

Fig. 3. Etch rate of ZnS:Mn and SiO_2 as a function of RF power.

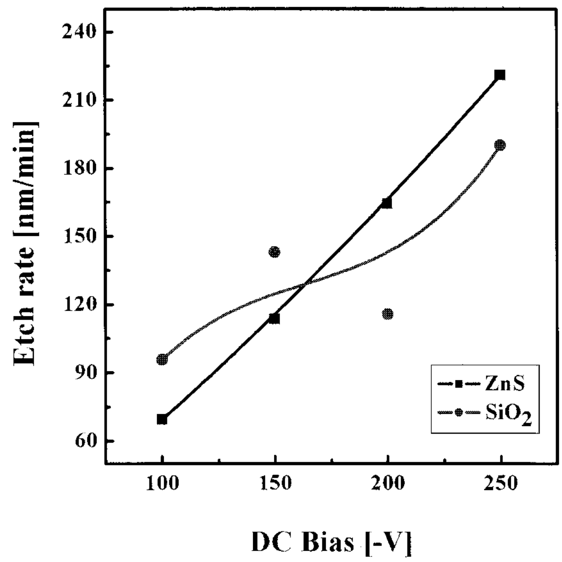

Fig. 4. Etch rate of ZnS:Mn and SiO_2 as a function of DC bias.

Other process condition was equal to Fig. 1. As the RF power increases from 600 W to 800 W, the etch rates of ZnS:Mn films increase from 147.3 nm/min to 191.0 nm/min. The etch rate of SiO_2 shows an increasing tendency (from 121.3 nm/min to 161.1 nm/min) with increasing RF power. As the RF power increased, the plasma becomes more dissociated and increases both the fluxes and densities for ions and radicals. The increased plasma density leads to increasing etch rate. This result indicates that the acceleration of chemical as well as physical etch mechanisms take place simultaneously[7-10].

Figure 4 shows the etch rates of ZnS:Mn and SiO_2 as a function of DC bias voltage while other parameters were kept at constant; the BCl_3/Ar gas mixture was 20 %, RF power was 700 W, and working pressure was 1 Pa, respectively. As DC bias voltage increased from -100 to -250 V, the etch rates of the ZnS:Mn and SiO_2 showed increasing tendency. The etch rates of ZnS:Mn increased from 69.5 nm/min to 220.9 nm/min. The etch rate of SiO_2 also increased from 65.6 nm/min to 190.0 nm/min. The increase etch rate behavior of ZnS:Mn can be explained by the fact that the ion bombardment energy increases with increasing DC bias voltage and results in the increasing sputtering yields both for main material and reaction products[11-13].

The etch rate as a function of working pressure is shown in Fig. 5. Other process condition was equal to Fig. 1. As the working pressure increase 0.5 Pa to 1 Pa, the etch rate of ZnS:Mn increased from 130.0 nm/min to 164.2 nm. As the working pressure increased further 1.5 Pa to 2 Pa, the etch rate of ZnS:Mn decreased from 155.4 nm/min to 104.5 nm/min. The decreased etch rate of ZnS:Mn at the 0.5 Pa can be explained by the disappearance

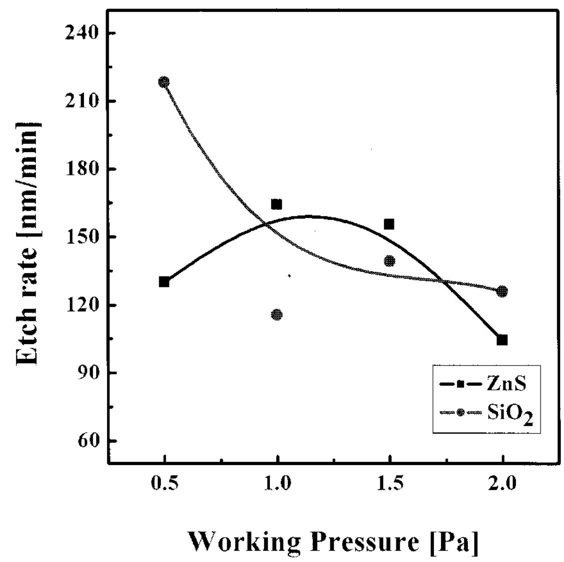

Fig. 5. Etch rate of ZnS:Mn and SiO_2 as a function of working pressure.

of chemical channel. However, the etch rate of SiO_2 showed a decreasing tendency from 218.3 nm/min to 126.0 nm/min with increasing working pressure from 0.5 Pa to 2 Pa. Since the mean free paths of species are inversely proportional to pressure, the reduction in potential translates into a lower energy ion flux to the substrate surfaces. That is, high pressures yield lower ion bombardment energies. These phenomena reveals that the chemical etch and the physical etch take place simultaneously.

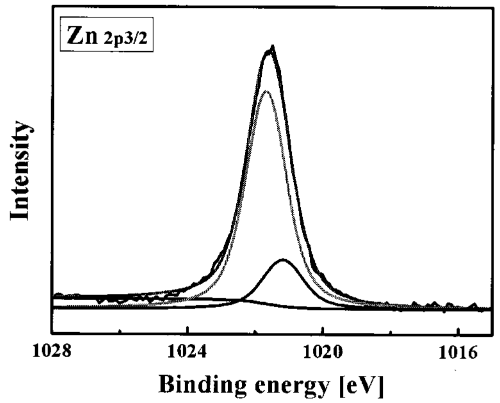

Fig. 6(a). Zn 2p XPS narrow scan spectra of ZnS:Mn surface etched with BCl_3/Ar plasma.

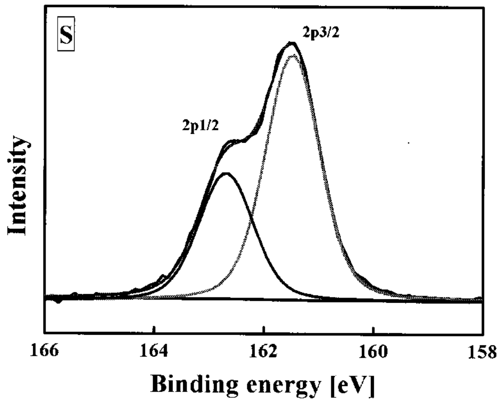

Fig. 6(b). S 2p XPS narrow scan spectra of ZnS:Mn surface etched with BCl_3/Ar plasma.

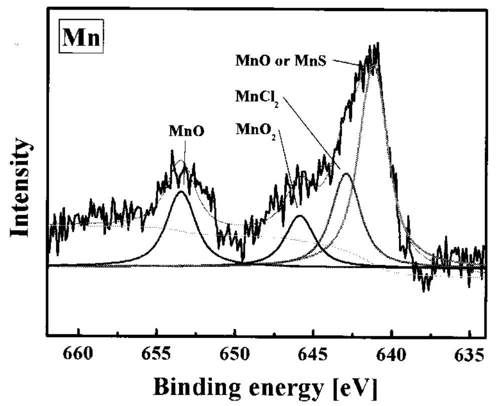

Fig. 6(c). Mn 2p XPS narrow scan spectra of ZnS:Mn surface etched with BCl_3/Ar plasma.

In order to study how Zn, S, and Mn combine with Cl radical, the XPS analysis was performed. The variation of Zn, S, and Mn peaks of etched ZnS:Mn surfaces is shown in Fig. 6. Figure 6(a) shows Zn $2p_{3/2}$ narrow scan spectra of the etched surface of ZnS:Mn thin films. The peaks at the binding energies of 1021.71 and 1021.21 eV in Fig. 6(a) can be assigned to ZnS and Zn of the Zn-S bond, respectively. $ZnCl_2$ has slightly lower vapor pressures, as shown in Fig. 2. This compound could easily vaporize from etched surface through the ion-stimulated desorption of the reaction products. Figure 6(b) represents S 2p narrow scan spectra. The peaks at the binding energies of 161.45 and 162.65 eV in Fig. 6(b) can be assigned to S $2p_{3/2}$ and S $2p_{1/2}$ of the Zn-S bond, respectively. The shapes of S 2p photoelectron peaks of the samples etched with Cl_2 plasma were exactly the same as that of as-deposited ZnS film. This result can be supported by the high vapor pressures of the possible sulfur-compounds such as S_2Cl_2(1 mmHg at -7.4 °C)[14]. As shown in Fig. 6(a) and (b), ZnClx and SCl_x spectra were not detected. This can be explained $ZnCl_x$ and SCl_x compound is dramatically removed because $ZnCl_x$ and SCl_x compound was volatile. Figure 6(c) shows that the Mn 2p narrow scan spectra can be resolved into the MnO(653.45 eV), MnO_2(645.85 eV), $MnCl_2$(642.96 eV) and MnS(641.26 eV) compounds. The accumulation of Mn was detected from XPS analysis. This result could be understood by the fact that $MnCl_2$ of low vapor pressure (10 mmHg at 778 °C) was supposed to be formed in the BCl_3 plasma, and could not be easily removed from the surface during etch process [14].

4. CONCLUSION

In this paper, we investigated the etching characteristics of ZnS:Mn thin films with using inductive coupled plasma of BCl_3/Ar. The maximum etch rate of ZnS:Mn thin films was 164.2 nm/min at a BCl_3(20)/Ar(80) gas mixing ratio. The etch rate of ZnS:Mn decreased as BCl_3 addition increased over 20 %. The etch rates for ZnS:Mn increased with increasing RF source power and DC bias voltage and decreasing working pressure. XPS analysis revealed that volatilization of both Zn and S occurs through the formation of metal chlorides. It was also detected that Mn was accumulated on the surface of ZnS:Mn after etching in BCl_3/Ar plasma. The etch data and XPS analysis confirmed the ion assisted chemical reaction in etching ZnS:Mn by the concurrence of chemical and physical pathways.

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