Etching Mechanism of Indium Tin Oxide Thin Films using Cl$_2$/HBr Inductively Coupled Plasma

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Dry etching characteristics of indium tin oxide films and etch selectivities over photoresist films were investigated using Cl$_2$/HBr inductively coupled plasma. From a Langmuir probe diagnostic system, it was observed that while the plasma temperature was kept nearly constant in spite of the change of the HBr mixing ratio, the positive ion density decreases rapidly with increasing the mixing ratio. On the other hand, a quadrupole mass spectrometer showed that the neutral HBr and Br species increased. The etching mechanism in the HBr/Cl$_2$ plasma was analyzed.

Keywords: Cl$_2$/HBr, ICP, ITO, QMS, Langmuir probe system

1. INTRODUCTION

As the displays such as thin-film transistor liquid crystal displays (TFT-LCDs) or electroluminescent displays (ELDs) are developed, the demand for transparent electrodes with high optical transmittance and ultra-low resistance in flat panel increases[1-3]. Among various electrode materials, indium tin oxide (ITO, 90 wt.% In$_2$O$_3$/10 wt.% SnO$_2$) with its low electrical resistance and high optical transparency in the visible range of the spectrum is one of the most available candidates. Because of these properties, ITO films are widely used in optoelectronic applications, such as transparent electrodes in liquid crystal displays[4], ferroelectric photo- conductor storage devices[5], and photovoltaic devices[6]. For the applications mentioned above, the development of an anisotropic dry etch process for the ITO thin films is an important task to be solved for obtaining an accurate pattern transfer and stable device parameters. For patterning this electrode, a wet etch process has been generally used, but the process has the problems such as reproducibility, isotropic etching, and the selective grain-boundary etching, etc.

To overcome the problems, dry etching processes have been developed using the fluorine-based (CF$_4$) and hydrogen-based (H$_2$, CH$_4$) chemistries[7-10]. One concern in the use of CH$_4$/H$_2$ chemistry is that α-C:H (amorphous hydrogenated carbon) or CH$_x$ polymer-like layers can be easily deposited, so that the excessive deposition of α-C:H films on the surface of the ITO film can impede a continued etching reaction. The α-C:H layers deposited during ITO etching, therefore, can limit the process window, in which the ITO layer is continuously etched[11-13]. The etch selectivity of ITO over photoresist films is also an important factor in many applications[13].

In this work, dry etching characteristics of ITO films and etch selectivities over photoresist films were investigated using Cl$_2$/HBr inductively coupled plasmas (ICP). At the same time, the etching mechanism of ITO thin films was studied using plasma diagnostic tools such as a quadrupole mass spectrometer (QMS) and a Langmuir probe diagnostic system (LP).

2. EXPERIMENTAL

ITO thin films were deposited on Si (100) substrate using the dc-magnetron sputtering of the (In$_2$O$_3$)$_{0.9}$:(SnO$_2$)$_{0.1}$ target. The process was held in Ar at a gas pressure of 5 mTorr and an input power of 80 W. The thickness of the ITO films was about 200 nm. The experiments were performed in a planar inductively coupled plasma (ICP) reactor. The reactor consisted of a cylindrical quartz chamber with a radius of 16 cm and a 5-turns copper coil located above 10 mm-thick horizontal quartz window. The coil was connected to a 13.56 MHz power supply. The bottom electrode was connected to another 12.56 MHz power supply to produce a negative dc bias voltage. Specially, in this work, the 12.56 MHz power supply connected to the bottom electrode was used to prevent the plasma instability. The experiments were performed under the fixed set of input parameters: a gas pressure of 6 mTorr, an input ICP power of 700 W, a bias power of 200 W and a total gas flow rate of 40 sccm while only the Cl$_2$/HBr mixing ratio was varied in the range from 0 % to 100 % HBr by adjusting the flow rates of the individual gases. The temperature of etched samples was stabilized at 18 ± 2 °C. The etched depths were measured using a surface profiler (Alpha-step 500, Tencor). The LP diagnostics was realized with a double probe (DLP2000, Plasmart Inc.) installed through the chamber wall-side view port. The probes were placed at 4 cm above the bottom electrode and centered in

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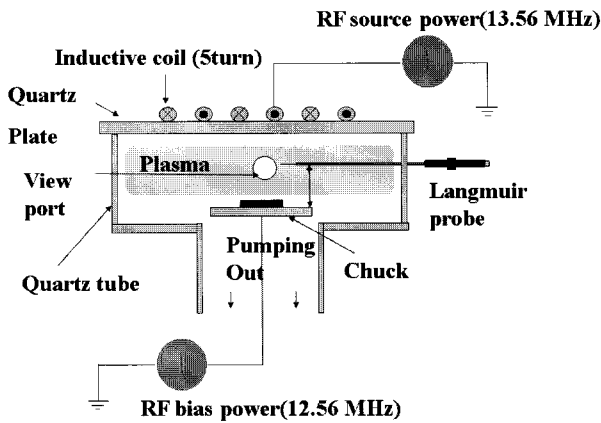* Author to whom corresponding should be addressed: electronic mail: kwonkh@korea.ac.kr

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 3. ITO etch rate and self bias voltage as a function of various Cl_2/HBr gas mixing ratio.

the radial direction. For the treatment of I-V curves in order to obtain electron temperature and total positive ion density, we used the software supplied by the equipment manufacturer[14]. The calculations were based on the double-probes theory developed by Johnson and Malter[15]. The quadrupole mass spectrometry (QMS) (EQP 150, Hiden Analytical) delivered the data on neutral species only.

3. RESULTS AND DISCUSSION

Figure 2 illustrated the influence of the Cl_2/HBr mixing ratio on plasma characteristics such as positive ion density and plasma temperature. As the HBr mixing ratio increases from 0 % to 100 %, the plasma temperature was obtained at the range from 3.41 eV to 3.73 eV. The deviation of the data was smaller than that in the case of a fixed HBr ratio. That is, it was explained that the temperature was kept nearly constant in spite of the change of the HBr mixing ratio. On the other hand, the positive ion density decreases rapidly in the range from $7.8 \times 10^{10}/cm^3$ to $5.44 \times 10^{10}/cm^3$. While the positive ion species in the Cl_2 plasma are mainly Cl_2^+ and Cl^+, HBr^+ is main species in the HBr plasma[14,16]. In the cited references, we can find out the threshold energies for HBr^+ and Cl_2^+ are 12.7 eV and 11.5 eV, respectively. From this data, we can explain why the positive ion density decreases with increasing the HBr mixing ratio. That is, the ionization rate for HBr gas seems to be lower than that for Cl_2 gas.
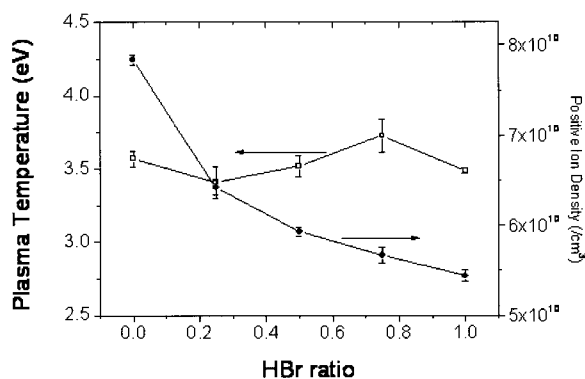
Figure 3 showed ITO etch rates and self bias voltages as a function of the Cl_2/HBr mixing ratio. While the self bias voltage increased from 310 V to 337 V with increasing the Cl_2/HBr mixing ratio at lower mixing ratio, the voltage decreased gradually from 337 V to 323 V at higher mixing ratio on the contrary. Meanwhile, the ITO etch rate increased monotonically in the range from 7.82 nm/min in pure Cl_2 up to 23.26 nm/min in pure HBr. This etch rate does not agree to the self bias voltage. Self bias voltages are of critical importance for plasma etching, since positive ions are accelerated toward the surface when entering a sheath.

Even though the self bias voltage decreased at the higher mixing ratio, the ITO etch rate gradually increased with the mixing ratio. This phenomenon means that the ITO etch rate are not determined only by the ion bombarding energy on the surface. On the other hand, it was checked in this experiment the ion density in the plasma decreased with increasing the mixing ratio. This phenomenon cannot also explain the increase in the etch rate with increasing the mixing ratio. We therefore investigated radicals in the plasma with the QMS.

Figure 4 illustrated the partial pressure of Cl_2, Cl, HBr, and Br which are the main neutral species in the Cl_2/HBr plasma.

In Fig. 4(a), we can find out the Cl_2 density gradually decreases with decreasing the Cl_2 gas ratio. This is natural due to the decrease in the Cl_2 ratio in the plasma. At the low HBr (that is, high Cl_2) ratio, a small portion of Cl_2 gas was dissociated. A significant portion of the chlorine was not dissociated in the plasma. Oppositely, at the high ration, the significant portion of the chlorine was dissociated into Cl radicals in the plasma. In Fig. 4(b), we can find out the increase in HBr and Br species in the plasma. This result indicates that the ITO etch rate is closely related to the density of neutral Br species in the plasma. In the Cl_2/HBr plasma, we can estimate the chemical compounds such as $InBr_x$ and $SnBr_x$ will be formed on the etched surface. $InBr_x$ is known to be the moderately or low volatile solid-state compounds (the lowest T_{mp} = of 220 °C is obtained for InBr), so that the role of thermally-activated (spontaneous) desorption of $InBr_x$ at surface temperatures below 100 °C can be negligible. $SnBr_4$ seems to be a volatile compound (T_{mp} = 29.1 °C) and therefore, it can be gasified spontaneously even at room temperature. Oppositely, the

Fig. 2. Positive ion density and plasma temperature as a function of various Cl_2/HBr gas mixing ratio.

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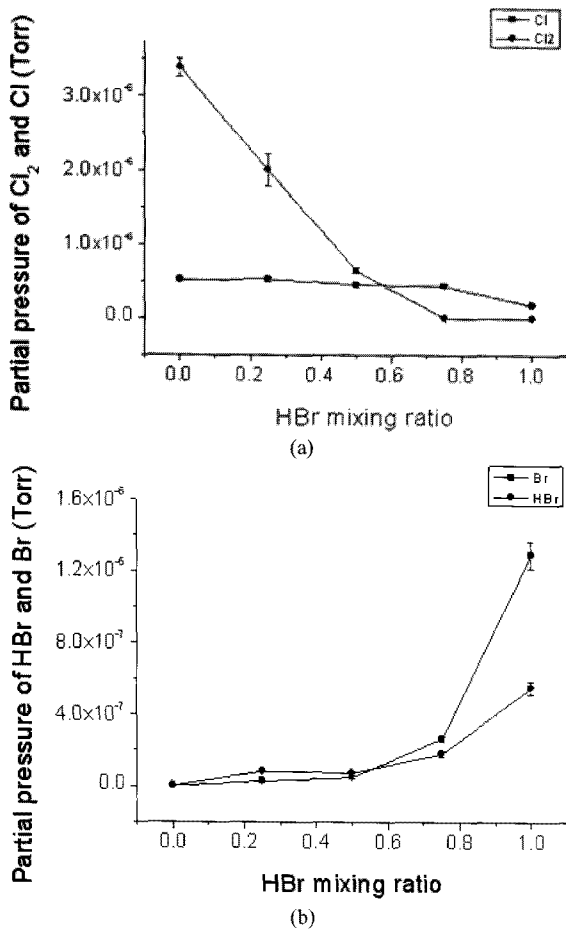
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Fig. 4. partial pressure of neutral species as a function of various Cl_2/HBr gas mixing ratio. (a) Cl and Cl_2, (b) HBr and Br

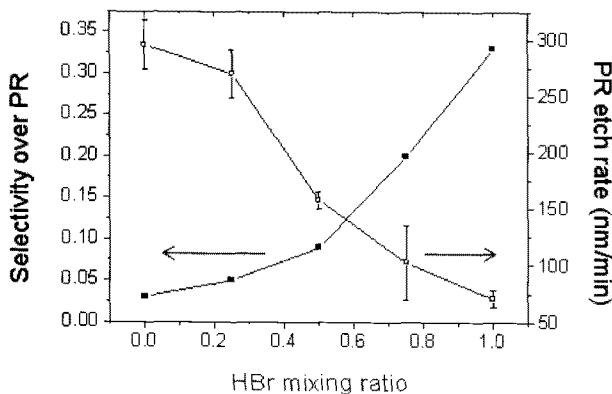Fig. 5. PR etch rate and selectivity as a function of various Cl_2/HBr gas mixing ratio.

volatility of $SnBr_2$ (T_{mp} = 215 °C) is much lower, so that one can assume a negligible contribution of spontaneous desorption compared with the ion-assisted one. Meanwhile, the ITO film is mainly composed of In_2O_3. That is, the rate-determining byproduct of the ITO etch in the HBr plasma is $InBr_x$. Meanwhile, in Fig. 3, the self bias voltages which range from 310 V to 337 V seem to be enough for removing the $InBr_x$ compounds from the surface.

Accordingly, the ITO etch mechanism in the HBr/Cl_2 plasma can be preliminary suggested as the ion-assisted chemical reaction where the role of ion bombardment includes only desorption of low volatile $InBr_x$ to provide the access of Br atoms to the etched surface.

Figure 5 plotted the photoresist selectivity and etch rate with various HBr mixing ratio. This figure showed that the photoresist etch rate decreased with increasing the ratio. The PR etch rate decreased monotonically in the range from 294 nm/min in pure Cl_2 up to 70 nm/min in pure HBr. As a result, the high HBr ratio is useful for obtaining the high selectivity over the PR.

4. CONCLUSION

Dry etching characteristics of ITO films and etch selectivities over photoresist films were investigated using Cl_2/HBr inductively coupled plasmas (ICP). The data using a Langmuir probe diagnostic system showed that the plasma temperature was kept nearly constant in spite of the change of the HBr mixing ratio. On the other hand, the positive ion density decreases rapidly.

While the self bias voltage increased from 310 V to 337 V with increasing the Cl_2/HBr mixing ratio at lower mixing ratio, the voltage decreased gradually from 337 V to 323 V at higher mixing ratio on the contrary. Meanwhile, the ITO etch rate increased monotonically with increasing the HBr ratio. At the same time, we can find out the increase in HBr and Br species in the plasma. This result indicates that the ITO etch rate is closely related to the density of neutral Br species in the plasma. On the basis of the data from the Langmuir probe system and the QMS, the ITO etch mechanism in the HBr/Cl_2 plasma can be preliminary suggested as the ion-assisted chemical reaction where the role of ion bombardment includes only desorption of low volatile $InBr_x$ to provide the access of Br atoms to the etched surface.

It was also observed that the PR etch rate decreased monotonically with the increase in the HBr mixing ratio. Accordingly, the high HBr ratio is useful for obtaining the high selectivity over the PR.

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