Characterization of H$_2$O- inductively coupled plasma for dry etching

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Abstract. We have demonstrated the discharge of the H$_2$O plasma by introducing water vapor to the process chamber. The H$_2$O plasma was characterized by optical emission spectrum analysis and mass spectrum analysis. We observed some species such as OH, H, O, and H$_3$O with these analysis methods. We expect that H$_2$O plasma etching is useful for dry etching process.

1. Introduction
In microfabrication techniques for optical or electron devices, dry-etching process of III-V compound semiconductors is useful technology for fine pattern fabrication of these devices. Usually, reactive gas is used as an etching gas in these processes. We have proposed the use of an I$_2$ crystal with high volatility as the solid source of etching gas in the process chamber for dry etching of InP [1]. We succeeded in an inductively coupled plasma (ICP) etching of InP using the solid source of iodine as a new simple dry etching process. In addition, we also succeed a dry etching process for GaAs using ICl$_3$ powder with high volatility as a solid source of chlorine [1]. As mentioned above, we have realized the solid source dry etching process. By the way, materials for the optical and electron devices are not only the compound semiconductors but also other materials such as fluoride or oxide. We think that the reactivity of H$_2$O (vapour) by presence of OH is useful for dry etching process. We would like to propose a novel dry etching process using H$_2$O. In H$_2$O processes, for example, Jimbo et al reported F$^+$ H$_2$O down stream ashing for removal of resist and sidewall film in Al etching [2]. We would like to propose a new dry etching process using liquid source of H$_2$O.

In this paper, we report on H$_2$O plasma characteristics of optical emission spectrum analysis and mass spectrum analysis.

2. Experimental Results
We used an ICP etching system (Samco RIE-101ip) as shown in Figure 1. We used a stainless circular plate (4” φ) as the sample tray. In this experiment, the sample holder temperature was kept at 200°C. We used H$_2$O (vapor) as an etching gas. The H$_2$O gas was supplied as water vapor through a mass flow controller using a water tank with a heating system.

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Figure 2 shows measured optical emission spectrum of the H\textsubscript{2}O at the position on the sample tray. We observed the emission of the plasma through a sapphire window. We used an optical fibre probe with a 0.5mm-\(\phi\) pinhole at the end of the food. The measured field was approximately 4 degrees [3]. The discharged conditions were H\textsubscript{2}O gas flow rates: 5sccm, ICP power: 100W and process pressure: 1 Pa. In this figure, it was found that the emission signals originated from OH (283 and 307nm), H (486 and 656nm) and O (777nm) was observed and the intensity of OH was much larger than those of H and O. It is considered that the H\textsubscript{2}O is dissociated in the plasma.

Figures 3 shows the mass spectrum of the neutral particles in the H\textsubscript{2}O-ICP without applying bias power. The discharged conditions were the same as Fig. 1. Some signals, such as H, H\textsubscript{2}, O, O\textsubscript{2}, OH, H\textsubscript{2}O and H\textsubscript{3}O were observed. It was also found that the H\textsubscript{2}O gas was dissociated in the plasma. It is interesting that H\textsubscript{3}O was observed in the H\textsubscript{2}O plasma.

In research fields of comets and the interstellar medium, some processes by photoionization and by
collision were known as reactions of H₂O. Some of reaction examples are as follows [4-6].

\begin{align*}
  \text{H}_2\text{O} + hv & \rightarrow \text{H} + \text{OH}. \quad (1) \\
  \text{OH} + hv & \rightarrow \text{H} + \text{O} \quad (2) \\
  \text{H} + hv & \rightarrow \text{H}^+ + e^- \quad (3) \\
  \text{O} + hv & \rightarrow \text{O}^+ + e^- \quad (4) \\
  \text{H}_2\text{O} & \rightarrow 2\text{H}^+ + \text{OH} + 3e^- \quad (5) \\
  \text{H}_2\text{O}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH} \quad (6) \\
  \text{OH}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH} \quad (7) \\
  \text{OH}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{O} \quad (8) \\
  \text{H}_2\text{O}^+ + \text{e}^- & \rightarrow \text{H}_2\text{O} + \text{H} \quad (9) \\
  \text{H}_2\text{O}^+ + \text{e}^- & \rightarrow \text{OH} + \text{H} + \text{H} \quad (10) \\
  \text{H}_2\text{O}^+ + \text{e}^- & \rightarrow \text{OH} + \text{H}_2 \quad (11) \\
  \text{O}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}^+ + \text{O} \quad (12)
\end{align*}

In addition, Pavlik and Skalny reported the following reactions on positive corona discharge in air [7].

\begin{align*}
  \text{H}_2\text{O} + \text{e} & \rightarrow \text{H}^+ + \text{OH}^- + \text{e} \quad (13) \\
  \text{O}_2 + \text{e} & \rightarrow \text{O}_2^+ + 2\text{e} \quad (14) \\
  \text{H}_2\text{O}^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH} \quad (15) \\
  \text{H}_2\text{O}^+ + \text{O}_2 & \rightarrow \text{H}_2\text{O} + \text{O}_2^+ \quad (16) \\
  \text{O}_2^+. \text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{OH} + \text{O}_2 \quad (17) \\
  \text{O}_2^+. \text{H}_2\text{O} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+.\text{OH} + \text{O}_2 \quad (18) \\
  \text{H}_3\text{O}^+.\text{OH} + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+.\text{H}_2\text{O} + \text{OH} \quad (19)
\end{align*}

As mentioned above, it is considered that there are a lot of complex reactions in H₂O plasma processes.

Figure 4(a) and 4(b) show the optical emission intensity of OH (a), H and O (b) as a function of ICP power. The plasma was discharged at a gas pressure of 1 Pa.

Figure 4(a) and 4(b) show the optical emission intensity of OH, H and O as a function of ICP power. The plasma was discharged at a gas pressure of 1 Pa. The emission intensity of these species increased with increasing the ICP power. It was found that the emission intensity of these species was dependent on the bias power. We also investigated the bias power dependence of the ion density.
Figure 5(a) and 5(b) show the optical emission intensity of OH, H and O as a function of process pressure. The plasma was discharged at an ICP power of 300W. The emission intensity of OH has a minimum value and that of H has a maximum value at 0.8 Pa, respectively. The emission intensity of O decreased slightly with the increasing process pressure.

The emission intensity of these species was not changed in the range of the flow rate between 1 and 5 sccm. We think that the sticking effect of H$_2$O to the surface of process chamber is very large.

3. Conclusions
In conclusion, we have demonstrated the discharge of the H$_2$O plasma by introducing water vapour to the process chamber. The H$_2$O plasma was characterized by the optical emission spectrum analysis and the mass spectrum analysis. We observed some species such as OH, H, O, H$_2$O and H$_3$O with both analysis methods. We think that it is also important to take account of the space plasma or the discharge in air for understanding of H$_2$O plasma. We expect that the H$_2$O plasma etching is useful for dry etching plasma.

In addition, we think that the OH plasma generated by using the proposed manner may be also useful for sterilization and UV light source.

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