한국전기전자재료학회 2004년도 하계학술대회 논문집

유도 결합 플라즈마를 이용한 MgO 박막의 식각특성

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The etching properties of MgO thin films in Cl_2/Ar gas chemistry

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Abstract

The metal-ferroelectric-semiconductor (MFS) structure is widely studied for nondestructive readout (NDRO) memory devices, but conventional MFS structure has a critical problem. It is difficult to obtain ferroelectric films like PZT on Si substrate without interdiffusion of impurities such as Pb, Ti and other elements. In order to solve these problems, the metal-ferroelectric-insulator-semiconductor (MFIS) structure has been proposed with a buffer layer of high dielectric constant such as MgO, Y_2O_3, and CeO_2. In this study, the etching characteristics (etch rate, selectivity) of MgO thin films were etched using Cl_2/Ar plasma. The maximum etch rate of 85 nm/min for MgO thin films was obtained at Cl_2(30%)/Ar(70%) gas mixing ratio. Also, the etch rate was measured by varying the etching parameters such as ICP rf power, dc-bias voltage, and chamber pressure. Plasma diagnostics was performed by Langmuir probe (LP) and optical emission spectroscopy (OES).

Key Words : Etching, MgO, Langmuir Probe, OES.

I. INTRODUCTION

Ferroelectric thin films have been widely studied as one of the materials for capacitor dielectric films in dynamic random-access memories (DRAMs) and ferroelectric random-access memories (FRAMs) and as gate insulators in metal-ferroelectric-semiconductor (MFS) structure [1, 2]. Among these, the MFS-FET is expected to be one of the future memory devices. However, this device suffers from interface states and material reaction between the ferroelectric thin film and the silicon substrate. Recently, A partial solution to this problem was reported that incorporates a proper insulating buffer layer between the ferroelectric and silicon, such as Y_2O_3, CaF_2, CeO_2, or $SrTiO_3$, MgO. In particular, MgO is one of the materials suitable for use as an intermediate layer because of its higher Poisson's ratio and lower Gibbs free energy than that of SiO_2.

In this study, MgO thin films were etched with Cl_2/Ar gas chemistries in inductively coupled plasma (ICP). Etching characteristics on the MgO thin films have been investigated in terms of etch rate and selectivity. To understand the etching mechanism, Langmuir probe (ESPION, Hiden Analytical) and optical emission spectroscopy (NTS-U101, NANOTEK 4) analysis were utilized for plasma diagnostic. Measurements of ion current density were carried out using the Langmuir probe, which showed the change of ion bombardment. Optical emission spectroscopy analysis was performed to analyze the behavior of active species as a function of gas mixing ratio.

II. EXPERIMENTAL

The MgO thin films were prepared on a (100) Si substrate by using sol-gel method. The MgO precursor solution was spin-coated on a substrate by using a spinner operated at 3500 rpm for 30 s. After coating, pyrolysis is followed on the hot plate maintained at 350 °C for 10 min to remove organic materials. The spin coating and drying was repeated to obtain MgO films of desired thickness. Amorphous films were sintered at 650 °C for 1 h to crystallize in a preheated furnace. The MgO films were etched in planar ICP system. The gas mixing ratio was varied to find the characteristics of etching. For these experiments, the total gas flow, chamber pressure, top rf power, bottom dc-bias voltage, and substrate temperature was 20 sccm, 10mTorr, 700W, -300 V and 30 °C, respectively. In addition, plasma etching of MgO films was investigated by changing the etching parameter including top rf power 500 ~ 800 W, dc-bias voltage to substrate -200 ~ - 350 V, and gas pressure 1 ~ 15 mTorr with the fixed Cl_2/Ar gas mixing ratio. The etch rate was measured by the surface profiler (KLA Tencor, a-step 500). Cl_2/Ar plasma was diagnosed by OES (NANOTEK4 NTS-U101). Langmuir probe measurement was performed using a single, cylindrical, and rf compensated probe (Hiden, ESPION). We used the software supplied by the equipment manufacturer for obtaining ion current density with the treatment of "voltage - current" traces.

III. RESULT AND DISCUSSION

For the characterization of etched MgO thin films in an ICP system, the MgO thin films, photoresist (PR), SiO_2 were etched as a function of Cl_2/Ar gas mixing ratio, ICP rf power, dc-bias voltage, and the chamber pressure. Figure 1 represents the etch rate of MgO, SiO_2, PR, and

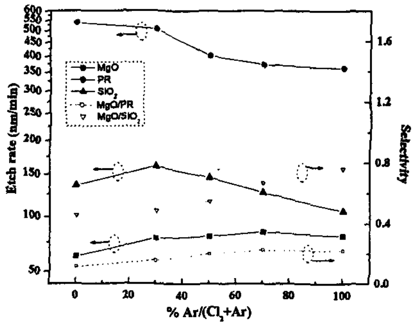

Figure 1. Etch rate and selectivity of MgO thin films as a function of Cl_2/Ar gas mixing ratio.

the selectivities of MgO to SiO_2 and PR as a function of Cl_2/Ar gas mixing ratio. The total flow rate of the gases was maintained at 20 sccm, ICP rf power/dc-bias voltage was 700 W/-300 V, chamber pressure was 10 mTorr, and substrate temperature was 30 °C. The etch rates of MgO thin films in pure Ar and in pure Cl_2 were found to be 80 and 65 nm/min, respectively. The maximum etch rate of the films was 85 nm/min when Ar 70% was added to Cl_2/Ar plasma. The etching process can be explained by two mechanisms such as physical sputtering and chemical reaction of Cl atoms formed in the plasma. The Ar ion bombardment in the Cl_2/Ar plasma played the role of not only physical sputtering but also destruction of metal bonds to cause a chemical reaction between metal and chlorine. The etch rate of pure Ar is larger than that of pure Cl_2. Accordingly, sputtering by Ar ions is more effective, and there is a little chemical enhancement by Cl_2. It is supposed that the etch products of MgO such as $MgCl_x$ are not particularly volatile, as the melting and boiling point of $MgCl_2$ is 714 °C and 1412 °C. Considering the etch rate of MgO, all subsequent experiments for the etching of MgO films were carried out with the etch gas of 30% Cl_2 in Cl_2/Ar plasma.

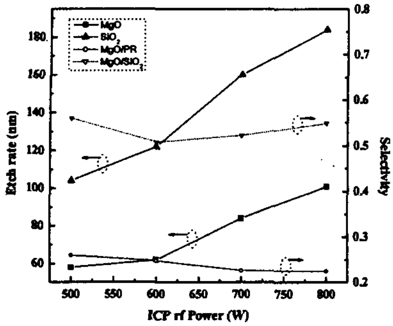

Figure 2. The effect of ICP rf power on the etch rate and the selectivity of MgO to PR and SiO_2.

Figure 2 shows the effect of ICP rf power on the etch rate of MgO, PR, and SiO_2 under 70% Ar in Cl_2/Ar plasma. As ICP rf power applied to the ICP antenna was raised from 500 to 800W, the etch rate of the MgO films increased from 58 to 101 nm/min. As increasing ICP rf power, plasma density becomes more dissociated and increases both reactive free radical number and ion number, which enhance the etch rates of MgO, PR, and SiO_2 [3].

The etch rate of MgO, PR, and SiO_2, and the selectivities of MgO to PR and SiO_2 are shown in Figure 3 as a function of dc-bias voltage. As

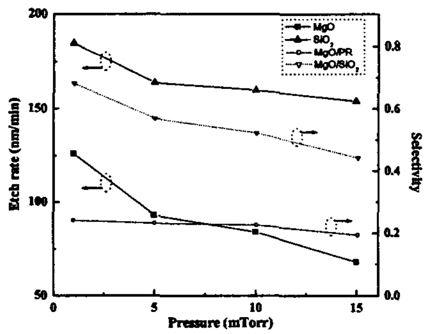

Figure 3. Etch rate and selectivity of MgO thin films as a function of pressure.

the dc-bias voltage increases from 250 to 350 V, the etch rate of MgO increases from 63 to 102 nm/min. As the dc-bias voltage was increased, the ion bombarding energy increased. Therefore, this result shows that the ion bombardment is more effective to etch MgO films.

The effect of chamber pressure on etch rate is shown in Figure 4. As the chamber pressure increases from 1 to 20 mTorr, the etch rate of MgO decreases from 126 to 68 nm/min. Since the mean free paths of species are inversely proportional to pressure, the recombination rate of ions decreases, then the number of ion that go toward the substrate surface increases and they have higher energies. That is, low pressure leads to higher ion bombardment energies.

Figure 5 illustrates the variation of ion current density as a function of Cl_2/Ar gas mixing ratio extracted from LP measurements. As Ar increases in Cl_2/Ar plasma, ion current density increases. It means that the increase of Ar content in Cl_2/Ar mixture leads to increase the number of ion. Because this etch process is more effective by physical component (ion bombardment), it seems that the reason why the etch rate increase is that ion current density increases. ICP rf power also increases ion current density. As mentioned above, the increase of ICP rf power causes the increase of

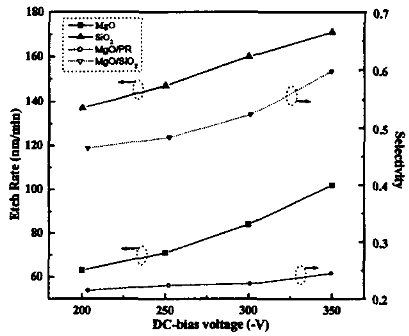

Figure 4. Etch rate and selectivity of MgO thin films as a function of dc-bias voltage.

reactive free radical number and ion number.

Therefore, higher ion current density could contribute the higher concentration of active species in the plasma and made the etch rate increase.

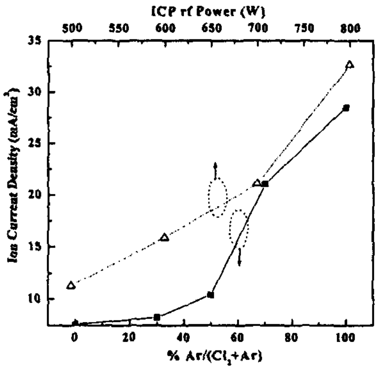

Figure 5. The variation of ion current density as a function of gas mixing ratio and ICP rf power.

Figure 6 shows the variation of emission intensities for Cl_2, Cl and Ar in Cl_2/Ar plasma which measured by OES. We estimated the atoms using the emission lines such as Ar (750.4 nm), Cl_2 (257.9 nm) and Cl (436 nm). It is well known that the main excitation mechanism for all lines is a direct electron impact processes. As Ar increases in Cl_2/Ar plasma, the emission intensities of Ar increase but that of Cl and Cl_2 atoms decrease. The emission intensity is a proportional to the volume density of atoms. This result confirms that Ar addition leads to increase ion current density and sputtering by Ar ions is more effective for MgO film.

IV. CONCLUSION

Etching characteristics of MgO thin films were investigated in terms of etch rate, selectivity using Cl_2/Ar plasma. Experiments were performed with variations of Cl_2/Ar gas mixing ratio, dc-bias voltage, and the chamber pressure. It was found that addition of Ar contents up to 70% leads the etch rate of MgO to increase in

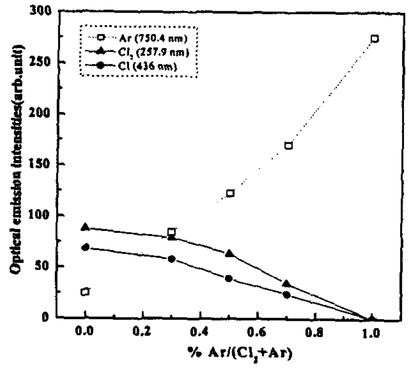

Figure 6. The optical emission intensity as a function of Cl2/Ar gas mixing ratio.

comparison with at Cl_2 only. The maximum etch rate of MgO films was 85 nm/min under 30% $Cl_2/(Cl_2+Ar)$ in 700 W, -300 V, 10 mTorr, and 30 ℃. LP analysis performed to investigate the variation of ion current density as a function of gas mixing ratio and ICP rf power. It showed that the increase of Ar addition enhanced ion bombardment and made the etch rate increase. These conclusions are consistent with the results of OES analysis.

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