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유도결합 플라즈마를 이용한 PST 박막의 식각 특성 및 이온 에너지 분포

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Etching characteristics of PST thin film and ion energy distribution using inductively coupled plasma

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Abstract - In this study, PST thin films were etched with inductively coupled $Cl_2/(Cl_2+Ar)$ plasmas. The etch characteristics of PST thin films as a function of $Cl_2/(Cl_2+Ar)$ gasmixtures were analyzed by using quadrupole mass spectrometer (QMS). Systematic studies were carried out as a function of the etching parameters, including the RF power and the working pressure. The maximum PST film etch rate is 56.2 nm/min, because a small addition of Cl_2 to the Cl_2/Ar mixture increased the chemical effect. It was proposed that sputter etching is the dominant etching mechanism while the contribution of chemical reaction is relatively low due to low volatility of etching products.

1. Introduction

In recent years, thin films made from high dielectric constant materials (high-k) have attracted great attentions for use in fabricating cell capacitors for high density dynamic random access memories (DRAMs) and microwave dielectric applications. Among the various high-k materials, the BST thin film was noticed as the most promising material for the capacitor dielectric of future high density DRAM because its high dielectric constant with good thermal stability and paraelectricity at normal operating temperature [1-3]. Although BST possesses a satisfactorily high-k, it was known that a post heat treatment at a high temperature was essential to obtain good electrical property. However, the heat treatment at high temperature can cause deleterious effects on an electrode, barrier metal, and contact plug [4].

Titanate compounds have been intensively studied to overcome the limitation of above drawbacks. Strontium titanate (ST) is one of the few titanates, which is cubic phase at room temperature. Tetragonal lead titanate (PT) films show higher dielectric constant than ST films at room temperature. But, the dielectric constant is lower than BST. The addition of lead into strontium titanate makes its dielectric constant higher and the temperature of crystallization lower [5, 6]. Therefore, PST thin film can be a promising material due to its high dielectric constant and paraelectricity at normal operating temperature. However, there is no report on the characteristics and mechanism of PST thin films during etching process.

In this study, inductively coupled plasma etching system was used for etching PST because of its high plasma density, low process pressure and easy control bias power.

2. Experimental Details

Experiments were carried out in planar ICP reactor. The reactor consists of cylindrical aluminum anodized chamber with diameter of 26 cm. One vertical view port on the chamber wall-side provides the installation of diagnostics tools such as QMS. A 3.5-turn copper coil, connected to 13.56 MHzpower generator, is located above the 24 mm-thick horizontal quartz window. The height of working zone, i.e. the distance between horizontal quartz window and bottom electrode, was 9 cm. The bottom electrode was connected to another 13.56 MHz asymmetric RF generator to control dc bias voltage. The Cl_2/Ar mixture was employed as enchants. Electronic grade gases comprising these mixtures were injected into the ICP source through mass flow controllers at a total flow rate of 20 sccm for Cl_2/Ar.

The PST thin films were etched as a function Cl_2/Ar plasma gas mixing ratio. Then, PST thin films were etched as functions of RF power, and working pressure, at which we obtained the maximum etch rate. The standard conditions were a working pressure of 15 mTorr, an ICP power of 700 W and DC bias voltage of 150 V. Etch rates were measured by using alpha-step surface profiler [KLA Tencor, alpha-step 500]. The dominants positive ion counts and energy distribution of the plasma were monitored by QMS [HIDEN, HAL 510].

3. Results and Discussion

The PST films were etched as a function of the Cl_2/Ar gas-mixing ratio in an ICP etching system. Figure 1 shows the etch rates of PST films and Pt as a function of the Cl_2/Ar gas mixing ration when total flow rate was maintained at 20 sccm. Other process conditions such as RF power, DC bias, working pressure, and substrate temperature were also maintained at 700 W, 150 V, 15 mTorr, 25 °C, respectively. As the gas mixing ratio increases to 20 % Cl_2, the etch rate of the PST film increases. However, when the gas mixing ratio exceeds more than 20 % Cl_2, the etch rate of the PST film decreases. This result confirms that PST film was etched not only by ion bombardment but also by chemical reaction. $PbCl_4$ (boiling point: 50 °C), $SrCl_2$ (boiling point: 1250 °C) and $TiCl_4$ (boiling point: 136

°C) are expected to form as etch product during the PST film etching with chlorine-based plasma chemistries [7]. But, due to the low volatility of $SrCl_2$compounds, the physical ion bombardment effect to enhance the ion assisted etch product desorption mechanism is required. Also, the etch rate of the Pt decrease as the Cl_2/Ar gas mixing ratio increases. Therefore we assume that in pure Cl_2plasma the etch rate is limited by the desorption of the reaction products from the etched surface. Addition of the Ar up to 80% increases the etch rate through the action of two mechanisms: 1) the acceleration chemical reaction owing to the ion-stimulated desorption of reaction products and 2) increasing of the contribution of physical sputtering. Nevertheless, when the Ar content exceeds 80%, the etch rate begin to fall down to the limit determined by the Ar^+ sputtering yield due to "disappearance"of chemical channel. In this case, chemical etching cannot give the noticeable contribution to the etch rate because the volume density of Cl atoms is too low.

To understand the roles of physical and chemical effects, and plasma tool surface interactions, we experimentally measured positive ion intensities and their energy distributions as the gas mixing ratio. For these purposes we used QMS analysis, and the results are shown in Figure 2 and 3. The dominant positive ions in the Cl_2/Ar plasma are Cl^+(35.45), Cl_2^+(70.9) and Ar^+(40). Figure 2 shows that the decreasing of Ar content in Cl_2/Ar mixtureleads to a direct proportional decreasing of intensity of Ar positive ion while Cl^+ and Cl_2^+positive ions were increased. Analysis of data reported above allows making some conclusions concerning etching mechanism of PST thin films. To our mind, the increasing of etching rate may be explained by two factors. First factor is connected with acceleration of physical sputtering of both main material such as PST film and surface layer of reaction products. The evident contribution of physical sputtering in etching process is confirmed by the fact that etching rate in pure Ar is sufficiently more than in Cl_2 gases. Second factor represents the sequence of first one and connected with acceleration of chemical interaction through the increasing of reaction probability and destruction of metal-oxide bonds. Also, these data was confirmed figure 3.

Figure 4 shows the effect of RF power on the etch rate of PST and Pt. $Cl_2/(Cl_2+Ar)$ of 20 % gas combination was used in the experiment and other process condition were the same as those shown in Fig. 1. As the RF power increases from 600 to 900 W, the etch rate of PST and Pt increases from 33.3 to 71.5 nm/min and from 39.6 to 110.9 nm/min, respectively. Figure 5 shows that the increase of PST etch rate with the increase of RF power appears to be from the increase of reactive chlorine radicals and ion energy intensity with the increase of RF power. Therefore, in this case, the acceleration of chemical as well as physical etch mechanisms take place simultaneously. That is why we obtained the increase of the etch rate for all the materials were examined.

3. Conclusion

In this study, PST thin films were etched with inductively coupled $Cl_2/(Cl_2+Ar)$ plasmas. The etch characteristics of PST thin films as a function of $Cl_2/(Cl_2+Ar)$ gas mixtures were analyzed by using quadrupole mass spectrometer (QMS). Systematic studies were carried out as a function of the etching parameters, including the RF power and the working pressure. The maximum PST film etch rate is 56.2 nm/min, because a small addition of Cl_2 to the Cl_2/Ar mixture increased the chemical effect. Addition of the Ar up to 80% increases the etch rate through the action of two mechanisms: 1) the acceleration chemical reaction owing to the ion-stimulated desorption of reaction products and 2) increasing of the contribution of physical sputtering. The optimum condition appears to be a 20 % $Cl_2/(Cl_2+Ar)$ gas mixture in the present work.

[Reference]

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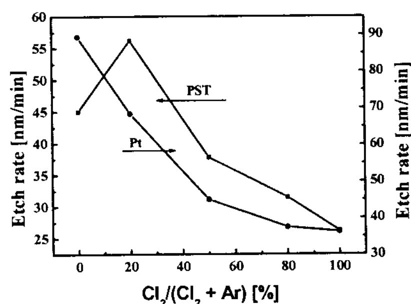


Figure1.EtchrateofPSTthinfilminCl-basedICPplasmaasafunctionofgasmixingratio.

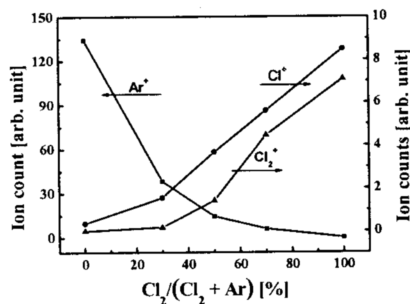
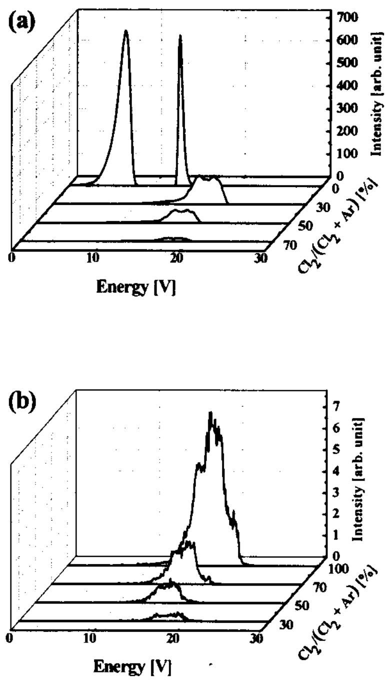


Figure2.IoncountsofdominantpositiveionsinCl-basedICPplasmaasafunctionofgasmixingratio.



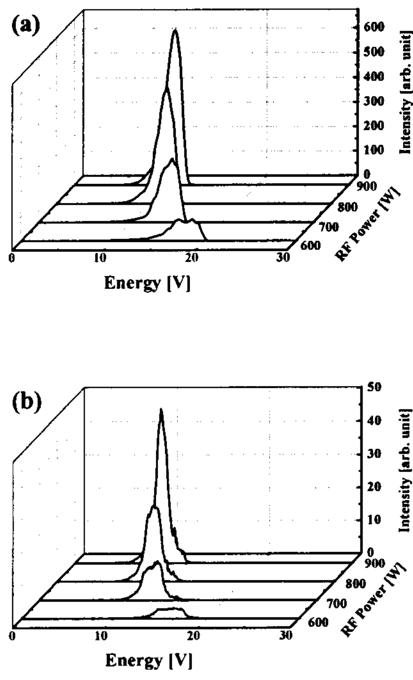


Figure3.Ionenergydistributionfunctionsof(a)$Ar^+$and (b)Cl^+fromaCl-basedICPplasmaasafunctionofgasmi xingratio.

Figure5.Ionenergydistributionfunctionsof(a)$Ar^+$and (b)Cl^+fromaCl-basedICPplasmaasafunctionofRFpo wer.

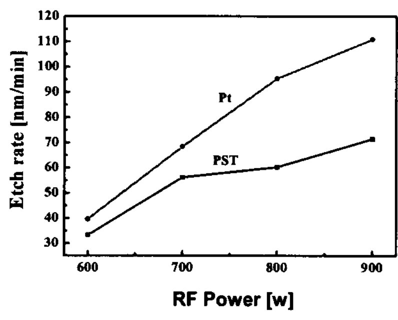


Figure4.EtchrateofPSTthinfilminCl-basedICPplas maasafunctionofRFpower.