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Etching Characteristics of (Ba, Sr)TiO_3 Thin Films in an Inductively Coupled Plasma

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1. Introduction

$BaTiO_3$ (BST) ferroelectric thin films have been attracting much attention as a large dielectric material for cell capacitance of highly integrated memory devices. Although the device applications provide a significant potential for improving the device performance, simplifying the structures and shrinking the device sizes, several problems must be overcome for application to be realized. These include improvement of the physical and electrical properties of the film and development of a process for dry etching of the BST films or electrode materials. The conventional reactive ion etcher may not applied to etch BST with a photoresist mask due to the poor selectivity. In this study, the etching characteristics of BST with Cl_2/CF_4, Cl_2/SF_6, and Cl_2/Ar gas mixtures are investigated and the etch response under various etching parameters will also be discussed.

2. Experimental

BST thin films of 1500Å thickness were deposited on Pt/Ti/SiO_2/Si substrates by metalorganic chemical vapor deposition or sol-gel process. All samples were patterned by a conventional photolithography method with a 1-μm-thick photoresist. Dry etching of BST films was investigated by using inductively coupled plasma (ICP) system, which consisted of a load-lock chamber, process chamber, and substrate susceptor assembly. The coil, which was connected to a 13.56 MHz RF power supply, was wound around the ceramic chamber to generate high-density plasma. A bias voltage induced by RF power at 13.56MHz was capacitively coupled to the substrate susceptor with capacitor to control ion energy. The etch rates were determined by alpha-step surface profilometer and etch profiles were examined by scanning electron microscopy (SEM).

3. Results and Discussion

To carry out this study, the GEMINI 2 software (developed by Thermodata company) [1] was used to determine the thermochemical equilibrium state of a system as a function of temperature. Table I tabulates the reactivity of Cl_2, CF_4, and SF_6 gases on BST at a pressure of 10 mTorr. These data exhibit that the BST etching needs more energy to form the volatility of $BaCl_2$ and $SrCl_2$. The effects of Ar, CF_4 and SF_6 gas concentration in a Cl_2 gas mixture on the BST etch rate are shown in Fig. 1. Very low etch rates of BST were obtained with in pure Ar, Cl_2 and gas mixtures. CF_4 and SF_6 were found to impede the etching process, presumably due to the redeposition effect. Since $BaCl_2$ and $SrCl_2$ have higher vapor pressures than BaF_2 and SrF_2, the BaF_2 and SrF_2 will produce a sidewall etch residue on patterned structures. Therefore, increasing the percentage of CF_4 or SF_6 in the gas mixture will result in a decrease in the BST etch rate. In the case of Cl_2/Ar gas mixture, the chemically assisted etch mechanism can improve these problems efficiently. A 30% Cl_2 in Cl_2/Ar gas mixture was found to yield optimum BST etch rate. Figure 2 shows the etch rate of BST thin film as a function of ICP coil power using a 30% Cl_2 in Cl_2/Ar gas mixture. With increasing the coil power, the plasma density increases so that the increased reactive free radicals and ions enhance the etch rate of BST. The etch rate of BST film was in the range of 3 to 25 nm/min. Figure 3 illustrates the effect of pressure and dc-bias on the etch rate of BST. As the gas pressure increases, the etch rate of BST decrease. It indicates that BST etches via physical sputtering. As the dc-bias increases, the etch rate of BST thin film almost increases linearly. The BST etching mechanism in a mixture of Cl_2/Ar can be described as follows. Under pure Ar etch condition, the redeposition effect of BST on photoresist was observed (Fig.4(a)). This indicates that the chemical enhancement to form volatility during the BST etching process is required. For etching with pure Cl_2, the low selectivity for photoresist and redeposition in fence were observed (Fig. 4(c)). The mechanism shows that some of radicals and ions in the plasma were decreased by the reaction of photoresist and the chemical reaction without physical enhancement would be removed inefficiency. Thus both chemical and physical etch would be required in the BST etch process. The optimum etching condition of BST thin film in this study was found at coil power of 600 watt, dc-bias voltage of 400 V and gas pressure of 10 mTorr with etching gas of 30%Cl_2 in Ar (Figs. 4(f)). Since the BST layer for future memory devices will be approximately 30 nm thick and cover an array of bottom electrode posts over a relatively large area, profile and etch rate requirements are not stringent [2]. Residue will be the most important plasma-etch issue for BST. So no residue and damage were the key point in this study.

4. Summary

The ICP etch behavior of BST has been characterized with Cl_2/CF_4, Cl_2/SF_6 and Cl_2/Ar gas mixtures. CF_4 and SF_6 were found to impede the etching process, presumably due to a competition between plasma deposition and etching. A local maximum in the etch rate occurred at 30% Cl_2 in Cl_2/Ar gas mixture, the chemical enhancement effect can reach maximum in this study. No residue and damage was found in the optimum recipe.

References

[1] Thermodata Co., St Martin d'heres, F-38000.
[2] S. P. Deornellas et.al. Solid State Technol., 41 (1998), p.53.

Table I Thermo equilibrium product of $BaTiO_3/SrTiO_3$ in 10 mTorr.

Gas	Reaction Temp.	Solid Product	Vapor Product
Cl_2	673.15K	TiO_2、$BaCl_2$、$SrCl_2$	Cl_2、O_2、Cl_1、CO、$TiCl_4$
	748.15K	TiO_2、$BaCl_2$、$SrCl_2$	Cl_2、O_2、Cl_1、$TiCl_4$、CO
	798K	TiO_2、$BaCl_2$、$SrCl_2$	Cl_2、O_2、Cl_1、$TiCl_4$、CO、$SrCl_2$、$BaCl_2$
CF_4	298.15K	TiF_4、BaF_2、SrF_2	CF_4、CO_2、TiF_4、COF_2
	898.15K	BaF_2、SrF_2	CF_4、TiF_4、CO_2、CO、COF_2、F、BaF_2、O_2
	998.15K	SrF_2、BaF_2	CF_4、TiF_4、COF_2、CO、CO_2、F、BaF_2、TiF_3、O_2、SrF_2
SF_6	298.15K	TiF_4、BaF_2、SrF_2	SF_6、SO_2F_2、TiF_4、SOF_4
	923.15K	SrF_2、BaF_2	SF_6、SOF_4、TiF_4、SF_5、SO_2F_2、SF_4、O_2、F、SOF_2、SO_2、F_2、BaF2
	998.15K	SrF_2、BaF_2	SF_6、SOF_4、TiF_4、SF_5、SO_2F_2、SF_4、F、O_2、SOF_2、F_2、SO_2、BaF_2、SF_3、SrF_2

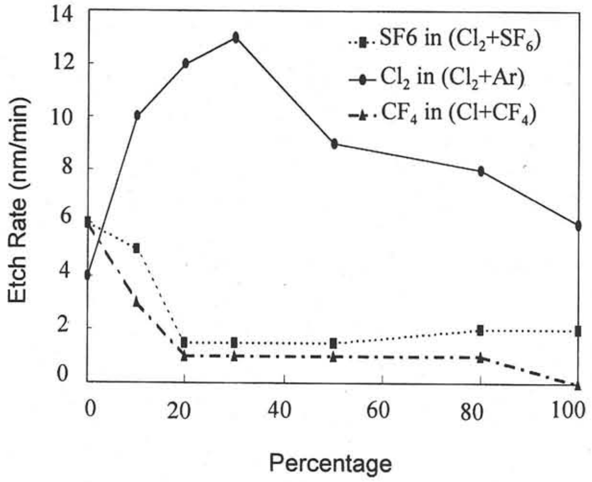

Fig.1 Etch rate of BST as a function of the gas concentration. The working pesssure is 15 mTorr, coil power 1000 W and dc-bias 500 V.

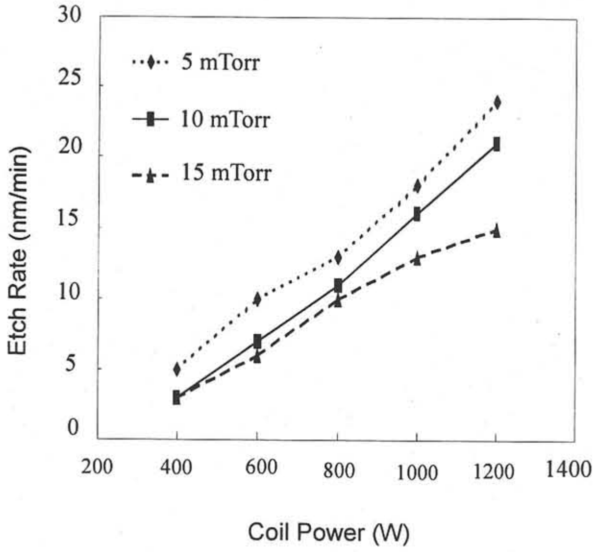

Fig. 2 Etch rate of BST as a function of the coil power. The gas used is 30% Cl_2 in (Cl_2+Ar) and the dc bias is 500 V.

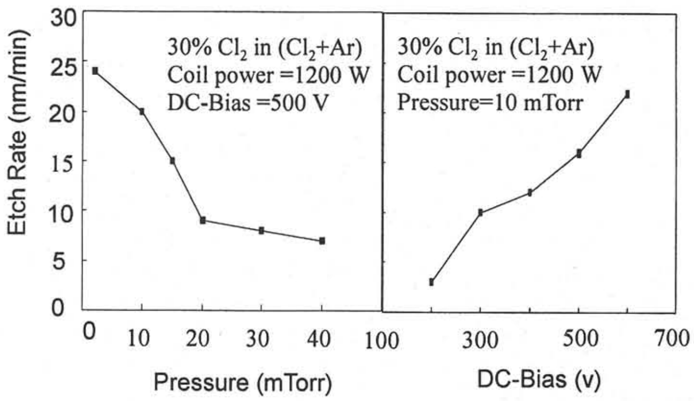

Fig. 3 Etch rate of BST as a function of the gas pressure and dc-bias.

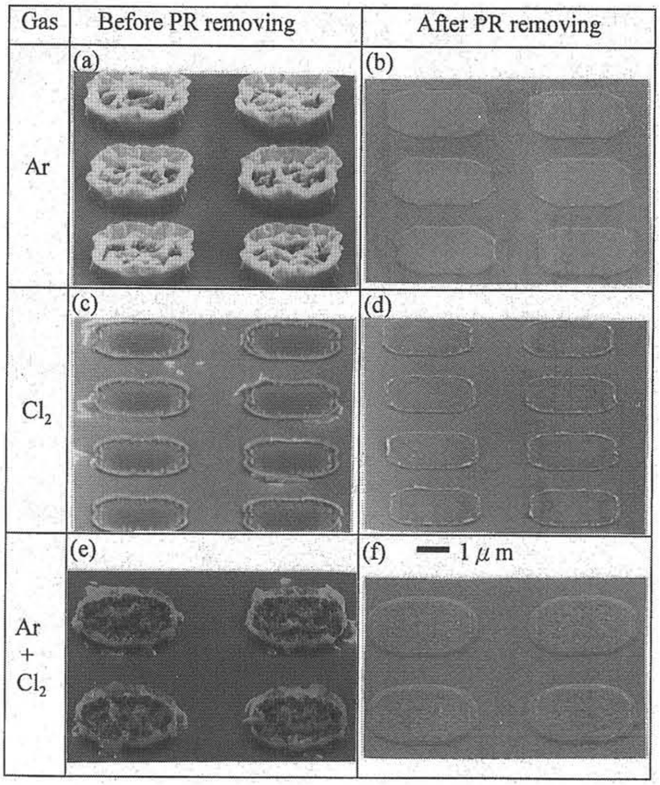

Fig. 4 SEM photographs of BST films etched at different conditions: coil power=600 W, dc-bias=400 V, pressure=10 mTorr.