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Thin Solid Films 471 (2005) 328–335

thin solid films

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Etching characteristics and mechanisms of $SrBi_2Ta_2O_9$ thin films in CF_4/Ar and Cl_2/Ar inductively coupled plasmas

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Received 14 May 2003; received in revised form 15 June 2004; accepted 15 June 2004
Available online 22 July 2004

Abstract

We investigated etching mechanism of the $SrBi_2Ta_2O_9$ (SBT) thin films using Cl_2/Ar and CF_4/Ar plasmas. The investigations were carried out through the analysis of the influence of gas mixing ratio on etch rate, plasma parameters and volume and surface chemistries. In both gas mixtures, increasing the Ar mixing ratio leads to an increase of the SBT etch rate, which reaches a maximum value at 80% Ar. The maximum etch rates are 970 and 1100 Å/min for Cl_2/Ar and CF_4/Ar plasmas, respectively. CF_4/Ar plasma exhibits higher electron temperature but lower electron density while for Cl_2/Ar plasma, these parameters are more sensitive to gas composition. The increase of Ar content in both gas mixtures causes monotonic changes of fluxes for all kinds of active species. Simplified description of ion-assisted etching mechanism indicates that a combination of physical sputtering and chemical etching activated by ion bombardment can account for the experimental data explaining the appearance of etch rate maximum as well as the differences in SBT etch rate in Cl_2/Ar and CF_4/Ar plasmas.

PACS: 52.75.Rx
Keywords: SBT; Etch rate; Electron temperature; Dissociation; Ion-assisted etching

1. Introduction

During last decade, the technology of microelectronics has involved use new materials aimed at substituting for traditional ones. The nearest example is the rapid development of nonvolatile ferroelectric random access memories (FRAM) using high-*k* ferroelectric thin films as the insulators for data storage capacitors [1]. Among the ferroelectrics were studied for FRAM device applications, the $SrBi_2Ta_2O_9$ (SBT) thin films are favorable materials. The reason is that they exhibit high dielectric constant and good fatigue endurance for up to 10^{11} switching cycles [1,2].

For the successful use of the SBT thin films in highly integrated FRAM devices, dry etching process is needed. At the same time, the development of etching process requires an understanding of the SBT etching mechanism in order to define the roles chemical and physical channels as well as the relationships between plasma parameters and process result. This will help to find optimal gas chemistry and process conditions, which support high etch rates, vertical profiles and the absence of sidewall residues. Unfortunately, the etching mechanism of SBT films is still not clear due to poor research experience for this material. Until now, there were only a few studies of the etching properties of SBT thin films using chlorine-based as well as fluorine-based plasma chemistries [3–8], including our earlier works [3,4,8]. In these works, most of the research has focused on the technological aspects while the investigations of etching mechanisms have received insignificant attention. The common problem was found is the low and different volatilities of metal chlorides and metal fluorides, which form masking layer on the etched surface and decrease the etch rate. However, although the existing literature data give similar results concerning the effects of basic operating conditions (pressure, input power, dc bias) on the SBT etch rate, they show contradictions for the influence of gas chemistry. For example, Refs. [5,6] reported the non-monotonic etch rate as a function of gas mixing ratio for Cl_2/Ar and CHF_3/Ar plasmas. Im et al. [5] obtained the maximum

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0040-6090/$ - see front matter
doi:10.1016/j.tsf.2004.06.126

etch rate of about 800 A/min corresponding to equal amounts of Ar and Cl_2 in Cl_2/Ar, while Seo et al. [6] give the maximum etch rate of 1650 A/min for 10% CHF_3/90% Ar. In contrast, Lee et al. [7] did not obtain the etch rate maximum but reported a constant etch rate of about 850 A/min in the range of 0–80% Ar in Cl_2/Ar mixture. Moreover, they found that the SBT etch rate in pure Cl_2 plasma exceeds the etch rate in pure Ar plasma. This fact contradicts the data of Refs. [4,5]. Unfortunately, the data from the works mentioned above related to various experimental conditions and etching systems making the results difficult to analyze together. All these facts have lead to a misunderstanding of the basic effects and obstruct the optimization of the etching process.

In this work, we investigated the etch mechanisms of SBT thin films using Cl_2/Ar and CF_4/Ar gas mixtures in an inductively coupled plasma (ICP) system through the analysis of the influence of gas mixing ratio on etch rate and plasma parameters. In order to understand the relationships between gas mixing ratios, volume densities of active species and etch rate, we used the combination of diagnostics methods such as Langmuir probes (LP), optical emission spectroscopy (OES) and secondary ion mass spectroscopy (SIMS).

2. Experimental details

The SBT thin films were deposited on Pt/Ti/SiO_2/Si substrates by metal organic decomposition (MOD). Precursors were strontium 2-ethylhexanoate, bismuth 2-ethyhexanoate and tantalum ethoxide with xylene as the solvent. Stock solutions with a mole ratio (Sr/Bi/Ta) of 0.8:2.4:2.0 were spun on the Pt layer, and then pre-baked on a hot plate at 400 °C for 10 min. The pre-baked films were annealed at 800 °C for 10 min under an oxygen atmosphere for crystallization. The final thickness of SBT films was about 300 nm.

Experiments were carried out in a planar ICP reactor [4,9]. The reactor chamber was made from stainless steel with Al_2O_3 coating of internal walls. A 3.5-turn copper coil, connected to 13.56 MHz power generator, is located above a 24-mm-thick horizontal quartz window. The bottom electrode was connected to another 13.56 MHz asymmetric rf generator to control dc bias voltage. All the experiments were carried out under the following fixed input parameters: total pressure of Cl_2/Ar or CF_4/Ar mixture of 15 mTorr, total gas flow rate of 20 sccm, input power of 700 W and dc bias voltage of -200 V while only the gas mixing ratio was varied.

The etch rates of SBT and PR (AZ1512, positive) were measured using the ellipsometry (L116B-85B, Gaertner Scientific) for the processing time of 1 min providing the stationary etching conditions. The initial thickness of the PR layer was about 1.2 μm. For the SBT etching, we developed the line striping of the PR with the line width/spacing ratio of 2:2 μm. The etch rate of the PR was also controlled in the independent measurements using the satellite sample. In all the cases, the samples size was about 2 cm^2.

Langmuir probe measurements were carried out using a single cylindrical, and rf-compensated probe (ESPION, Hiden Analytical), which was placed in the center of the reactor working zone both in axial and radial directions. For the treatment of I–V characteristics aimed at obtaining electron temperature, electron and ion densities, we used software supplied by the equipment manufacturer. OES measurements were carried out using a grating monochromator (NTS-U101, Nanotek) with the wavelength scope of 200–800 nm. The installation of diagnostics tools was provided through a vertical view port on the chamber wall side. Chemical states on the surface of the etched SBT films were investigated SIMS (CAMECA IMS6F).

3. Results and discussion

When a binary mixture of chemical active gas with noble gas is used for the etching, there are two main factors affecting the etch rate. The first is "volume chemistry" represented by the variations of the fluxes of active species on the etched surface. These fluxes depend on volume densities of corresponding particles resulted from the balance between formation and decay processes both in plasma volume and reactor walls. The second is "surface chemistry", which works through the reaction probability and sputtering yields for main material as well as for low-volatile reaction products. In this situation, gas mixing ratio seems to be a key parameter to understand etches mechanism because it reflects the transition between chemical and physical etching.

Before analyzing the etching results, lets overview the properties of SBT films influencing etching behavior in chemical active system. Kim and Kim [4] and Seo et al. [6] already reported that SBT components form a low volatile metal chlorides and metal fluoride. Actually speaking, to characterize the volatility, the data concerning the saturated vapor pressures are needed. Unfortunately, these data are absent and we can refer only for the simple qualitative correlation between volatilities and melting points for the corresponding compounds [4,10]. However, Fig. 1 shows that the etching products of SBT both using chlorine-containing and fluorine-containing plasmas are really hardly volatile compounds. That is why, we expect the contributions of thermal desorption and thus spontaneous chemical etching to be negligible while the etching process can be represented by the combination of ion-assisted chemical reaction and physical sputtering. Additionally, considering the data represented in Fig. 1, we can expect that pure Cl_2 plasma will provide higher etch rate compared with pure CF_4 plasma.

Fig. 2 shows the etch rate of SBT thin films and the etch selectivity of SBT over PR as a function of the Ar mixing