Available online at www.sciencedirect.com
SCIENCE DIRECT
Thin Solid Films 474 (2005) 267–274
thin solid films
www.elsevier.com/locate/tsf

Etching characteristics of $Pb(Zr,Ti)O_3$ thin films in Cl_2/Ar and CF_4/Ar inductively coupled plasmas: effect of gas mixing ratios

A.M. Efremov, Dong-Pyo Kim, Chang-Il Kim*

School of Electrical and Electronic Eng., Chung-Ang University, 221, Huksuk-Dong, Dongjak-Gu, Seoul 156-756, South Korea

Received 14 August 2003; received in revised form 27 April 2004; accepted 17 August 2004
Available online 25 September 2004

Abstract

The investigation of $Pb(Zr,Ti)O_3$ (PZT) etching mechanism in both Cl_2/Ar and CF_4/Ar plasmas was carried out. It was found that, in CF_4/Ar plasma, etch rate has a maximum at 80% Ar, while for Cl_2/Ar plasma, etch rate keeps a constant value up to 40% Ar. The volume densities and fluxes of active species in both gas mixtures derived from the zero-dimensional (0-D) plasma models change in same manner while a nonmonotonic behavior was not observed. However, the analysis of surface kinetics confirmed the possibilities of nonmonotonic etch rate behavior in both gas mixtures due to a concurrence of physical and chemical pathways in ion-assisted chemical reaction.

PACS: 52.77.Bn
Keywords: PZT; Etch rate; Electron temperature; Dissociation; Ion-assisted etching

1. Introduction

During the last decade, a lot of new materials were involved into a fabrication of memory devices aimed at overcoming limits resulted from conventional Si-based technology. Particularly, some ferroelectric thin films attract an attention as the insulating material for data storage capacitors for random access memories. Due to advanced dielectric properties of ferroelectric thin films, ferroelectric random access memories (FRAMs) provide smaller element size and thus, it helps to achieve higher data storage density [1]. Among ferroelectric thin films studied for FRAM device applications, $Pb(Zr,Ti)O_3$ (PZT) has an advantages of high dielectric constant as well as bistable polarization [1,2]. Therefore, the development of anisotropic etching process for PZT thin films is an important task.

Until now, there were several works devoted to the investigations of etching properties of the PZT thin films using fluorine- and chlorine-based plasma chemistries [3–8]. Summarizing published data, current situation may be characterized as follows. Unfortunately, in previous works, a main effort was applied to solve technological problems (etch uniformity, etch profile, etc.), while the etch mechanism, i.e., fundamental relationships between processing parameters, gas phase composition has received insufficient attention. In our opinion, there are two problems which make the etch mechanism of PZT to be not clear. First is that the etching data from various works related to various experimental conditions and etching systems make the results difficult to compare. Secondly, the existing literature data give similar results concerning the effects of basic operating conditions (pressure, input power, direct current (dc) bias) on the PZT etch rate, but show contradictions for the influence of gas chemistry. For example, Chung [6] reported that the addition of Ar to Cl_2/C_2F_6 (9:1) plasma keeps the PZT etch rate a constant up to 80% Ar. Similar results were obtained by Efremov et al. [8] for Cl_2/Ar plasma in inductively coupled plasma (ICP) system. On the contrary, Refs. [2,4,7] reported about nonmonotonic etch rate behavior as a function of gas mixing ratio in a binary gas mixtures. Chung et al. [4] obtained a maximum etch rate for 60% Ar in HBr/Ar plasma while Kang et al. [2] and Lee

* Corresponding author. Tel.: +82 28205334; fax: +82 28129651.
E-mail address: cikim@cau.ac.kr (C.-I. Kim).

0040-6090/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2004.08.023

et al. [7] reported a maximum etch rate in Cl_2/Ar plasma for 20% and 10% Ar, respectively. As an explanation for etch rate maximum, they give only a qualitative suggestions about the concurrence of chemical and physical etch mechanisms. Finally, Suchaneck et al. [3] show both non-monotonic and monotonic etching rate behaviors corresponding to the different input power conditions for CF_4/Ar plasma in a reactive ion etching reactor. Therefore, the problem of gas chemistry is a key problem to understand the PZT etch mechanism.

In this work, we investigated etching characteristics and mechanisms of PZT thin films using Cl_2/Ar and CF_4/Ar gas mixtures in an ICP system. Etching characteristics were investigated in the terms of PZT etch rate as a function of gas mixing ratios. Plasma diagnostics were performed by Langmuir probe measurements. To understand the etching mechanism, the models of volume and surface chemistry were developed.

2. Experimental and modeling

2.1. Experimental details

The PZT thin films were fabricated by sol–gel process on the Pt/Ti/SiO_2/Si substrates. The primary sol–gel solution was prepared from lead acetate-trihydrate, zirconium *n*-propoxide, and titanium isopropoxide. 2-Methoxyethanol was used as the solvent. The precursor PZT solution had the molar ratio of Pb/(Zr+Ti)=1.1 and Zr/Ti=53/47. The precursor solution was spin-coated for 30 s on the Pt/Ti/SiO_2/Si(100) substrates using a spinner operated at 3500 rpm. After the spin coating, the PZT films were involved in pyrolysis (10 min, 300 °C) to remove organic materials. The spin coating/drying cycles were repeated several times to obtain the final thickness of PZT films of about 300 nm. Finally, the PZT films were annealed in O_2 atmosphere (60 min, 650 °C) to crystallize them into the perovskite structure.

Both etching experiments and plasma diagnostics were performed in a planar ICP reactor described in our earlier works [9,10]. Cylindrical working chamber (∅ 26 cm) was made from stainless steel with Al_2O_3 coating inside. On the topside, horizontal quartz window separates the chamber and 3.5-turn copper coil, connected to 13.56-MHz power generator. On the bottom, an electrode used as substrate holder was connected to another 13.56-MHz asymmetric rf generator to control dc bias voltage. All the experiments were carried out under fixed input parameters: total pressure 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 Ar mixing ratio in both Cl_2/Ar or CF_4/Ar mixing ratio was varied. Temperature of the sample was stabilized at 30 °C.

The etch rate of PZT was measured using the ellipsometry (L116B-85B, Gaertner Scientific) for the processing time of 1 min providing the stationary etching conditions. The samples size was about 2 cm^2. To measure etch rate, we developed the line striping of the photoresist (PR; AZ1512, positive) with the line width/spacing ratio of 2:2 μm. The initial thickness of the PR layer was about 1.5 μm.

Plasma diagnostics was represented by Langmuir probe measurements. For this purpose, we used a single cylindrical and rf-compensated probe (ESPION, Hiden Analytical), which was installed through a vertical view port on the chamber wall-side and placed in the center of the reactor working zone both in axial and radial directions. For the treatment of "voltage-current" traces aimed at obtaining electron temperature and electron density, we used software supplied by the equipment manufacturer.

2.2. 0-D model for Cl_2/Ar and CF_4/Ar plasmas

To analyze the influence of gas mixing ratios on volume densities and fluxes of plasma active species, we applied elements of zero-dimensional (0-D) plasma model [11–13], assuming the Maxwellian electron energy distribution function (EEDF) and quasi-stationary approximation for volume kinetics [9,10]. To simplify the kinetic scheme for CF_4, we considered for well-known facts, which were repeatedly reported in literature. Accordingly, we assumed CF_4 molecules to be a main source of fluorine atoms in plasma volume, while the densities of unsaturated CF_x radicals are sufficiently lower than CF_4 density [14,15]. We assumed also that, in CF_4-rich plasma, dominant positive and negative ions are CF_3^+ and F^-, respectively [16,17].

According to Refs. [10,14,18], volume densities of chlorine and fluorine atoms may be estimated from kinetic balance equations:

$$\left(2k_{\mathrm{dis}}^{\mathrm{Cl_2}}+k_{\mathrm{di}}^{\mathrm{Cl_2}}+k_{\mathrm{da}}^{\mathrm{Cl_2}}\right)n_{\mathrm{e}}n_0(1-\delta)\approx\left(\gamma_{\mathrm{Cl}}\frac{D_{\mathrm{Cl}}}{\lambda^2}+\frac{1}{\tau_{\mathrm{res}}}\right)n_{\mathrm{Cl}} \quad (1)$$

$$\left(k_{\mathrm{dis}}^{\mathrm{CF_4}}+k_{\mathrm{di}}^{\mathrm{CF_4}}\right)n_{\mathrm{e}}n_0(1-\delta)\approx\left(\gamma_{\mathrm{F}}\frac{D_{\mathrm{F}}}{\lambda^2}+\frac{1}{\tau_{\mathrm{res}}}\right)n_{\mathrm{F}} \quad (2)$$

where k—rate coefficients for the processes specified in Table 1; n_e—electron density; n_0—total density of neutral particles; δ—fraction of Ar in gas mixtures; τ_{res}—residence time; γ_{Cl} and γ_F–probabilities of heterogeneous recombination for chlorine atoms ($\gamma_{Cl}\approx 0.2$ from Refs. [18,19]) and for fluorine atoms ($\gamma_F\approx 0.02$ from Ref. [20]); D_{Cl} and D_F—effective diffusion coefficients [10,11]; and λ—effective diffusion length [11,12]. The combination $\gamma D/\lambda^2$ in the right-hand side (RHS) of Eqs. (1) and (2) represents the rate coefficient of heterogeneous decay for chlorine or fluorine atoms assuming first-order recombination kinetics as well as diffusion transport of atoms to reactor walls [10,21,22].