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On the etching mechanism of ZrO_2 thin films in inductively coupled BCl_3/Ar plasma

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Abstract

The etching mechanism of ZrO_2 thin films in BCl_3/Ar plasma was investigated using a combination of experimental and modeling methods. It was found that an increase in the Ar mixing ratio causes the non-monotonic behavior of the ZrO_2 etch rate which reaches a maximum of 41.4 nm/min at about 30–35% Ar. Langmuir probe measurements and plasma modeling indicated the noticeable influence of a BCl_3/Ar mixture composition on plasma parameters and active species kinetics that results in non-linear changes of both densities and fluxes for Cl, BCl_2 and BCl_2^+. From the model-based analysis of surface kinetics, it was shown that the non-monotonic behavior of the ZrO_2 etch rate can be associated with the concurrence of chemical and physical pathways in ion-assisted chemical reaction.
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1. Introduction

High dielectric constant (high-k) materials, such as ZrO_2, Ta_2O_5, HfO_2 and TiO_2, have attracted a great attention to substitute for SiO_2 as a gate dielectric material for sub-0.1 μm complementary metal oxide semiconductor (CMOS) technology [1–6]. Among the materials mentioned above, ZrO_2 is one of the most attractive ones combining such favorable properties as a high dielectric constant ($k = 20$–25), wide bandgap (5–7 eV) as well as a close thermal expansion coefficient with Si that results in good thermal stability of the ZrO_2/Si structures. Therefore, the development of an anisotropic "dry" etching process for ZrO_2 thin films is an important problem to be solved for obtaining a small feature size as well as an accurate pattern transfer.

Until now, there were only a few works devoted to the investigations of the etching behavior of the ZrO_2 thin films using chlorine-based plasma chemistries. Particularly, Sha and Chang reported on the etch process of ZrO_2 thin film in both Cl_2 and Cl_2/BCl_3 [7–9] plasmas in an electron cyclotron resonance (ECR) reactor. Also, Pelhos et al. investigated the etch behavior of $Zr_{1-x}Al_xO_y$ thin film in Cl_2/BCl_3 plasma [10]. From these works, it can be concluded that the ZrO_2 etch rate is generally limited by the low volatility of Zr chlorides, but the process can be accelerated by the addition of BCl_3 that helps to volatilize oxygen from the oxide. The maximum ZrO_2 etch rate obtained in Ref. [8] was about 15 nm/min for 40% BCl_3/60% Cl_2 plasma. It is important to note that, although the mentioned works provide the information on regard to the dependences of the ZrO_2 etch rate on operating conditions (pressure, input

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power, bias power), the relationships between process parameters, plasma chemistry and surface kinetics were not explored well. Particularly, Sha and Chang [9] attempted to build the phenomenological model for the ZrO_2 etch process in BCl_3/Cl_2 plasma and obtained a relatively good agreement between measured and model-predicted etch rates. However, this model was rightly criticized by Stafford and Margot [11] because of both excess of free fitting parameters and pure agreement with the ion-assisted chemical etch mechanism. That is why, in fact, the etch mechanism is not clearly understood and this retards the development and optimization for the ZrO_2 etch process.

In this work, we investigated the etch mechanism of ZrO_2 thin films in an inductively coupled plasma (ICP) system with BCl_3/Ar gas chemistry. The BCl_3 was chosen as an active gas because it is widely used for the etching of the materials covered by the native oxides due to the effective extraction of oxygen in the form of BCl_xO_y compounds [12]. As the main parameter, we selected a BCl_3/Ar mixing ratio because it reflects the transition between chemical and physical etching and thus, provides better understanding of the etch mechanism. In order to analyze the ZrO_2 etch mechanism, the models of plasma chemistry and surface kinetics were developed.

2. Experimental and modeling details

2.1. Experimental setup and procedures

The 130-nm-thick ZrO_2 films were deposited on Si (1 0 0) substrates at 150 °C by a plasma-enhanced atomic layer deposition (PEALD) method. The detailed description on both the deposition method and operating conditions are given in Ref. [13]. Si (1 0 0) substrates were used to determine ZrO_2/Si selectivity.

Etching experiments were performed in a planar ICP reactor (Fig. 1). The reactor consisted of a cylindrical quartz chamber with a radius (r) of 16 cm and a 5-turn copper coil located on a 10-mm-thick horizontal quartz window. The coil was connected to a 13.56 MHz power supply. The distance between the quartz window and bottom electrode (l) used as a substrate holder was 12.8 cm. The bottom electrode was also connected to a 13.56 MHz power supply to control the dc bias voltage on the substrate. During the etch process, the temperature of the substrate holder was held at 17 °C by the circulation of deionized water. The etching conditions were: a total gas flow rate (q) of 60 sccm, an operating pressure (p) of 4 mTorr, an input ICP power (W) of 500 W and bias power (W_{dc}) of 100 W. High quality gases of ultra-pure BCl_3 (99.999%) and Ar (99.999%) were used. The BCl_3 mixing ratios were varied by adjusting the partial flow rate of the mixture components. The etched ZrO_2 samples had an area of 2×2 cm^2. To determine the etch rate and etch selectivity, the etched depths of ZrO_2 and Si were measured using a surface profiler (Alpha-step 500, Tencor). For this purpose, the we developed the line striping of the photoresist (PR) (AZ1512, positive). The initial thickness of the PR layer was about 1.2 μm.

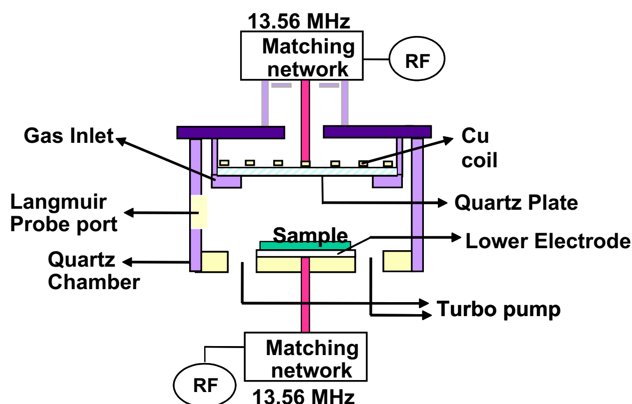

Fig. 1. Schematic drawing of the ICP etching reactor.

Plasma diagnostics were performed by double Langmuir probe (DLP2000, Plasmart Inc.) measurements. The probes were installed through the view-port on the side wall of the reactor chamber and centered in a radial direction. For the treatment of voltage–current curves aimed to obtain electron temperature and ion density we used the software supplied by the equipment manufacturer.

2.2. 0-Dimensional model for BCl_3/Ar plasma

To obtain the data on the densities and fluxes of plasma active species, we used a simplified global (0-dimensional) model with a Maxwellian electron energy distribution function (EEDF) and with a quasi-stationary approximation for the volume kinetics [14,15]. The applicability of the Maxwellian approximation for EEDFs in BCl_3, BCl_3/Cl_2 and Ar low-pressure ($p < 50$ mTorr) inductive discharges was illustrated in Refs. [16,17] by an outstanding agreement between plasma diagnostics data and modeling results. Also, our model accounts for some well-known facts, which were previously reported in the literature for BCl_3 ICP: (1) the dominant neutral ground-state dissociation products are Cl and BCl_2 [18,19]; (2) the main source of Cl atoms is the electron impact dissociation of BCl_3 molecules [16]; (3) the dominant type of negative ion is Cl^- [15]; (4) the dominant types of positive ions are BCl_2^+ and Cl^+ [16,19]. The list of processes taken into account by the model is specified in Table 1.

Volume-average densities of neutral ground-state species were estimated using the balance equations of chemical kinetics written as follows:

$$(k_1 + 2k_2 + k_3 + 2k_4)n_e n_{BCl_3} = (k_{11} + 1/\tau_R)n_{Cl}, \quad (1)$$

$$(k_1 + k_5 + k_6)n_e n_{BCl_3} = (k_{12} + 1/\tau_R)n_{BCl_2}, \quad (2)$$

$$n_{BCl_3} \approx n_0(1 - \delta)(T_0/T) - 0.5(n_{Cl} + n_{BCl_2}), \quad (3)$$

$$n_{Ar} = n_0\delta(T_0/T), \quad (4)$$

where k are the rate coefficients for the processes specified in Table 1, τ_R is the residence time, T is the gas

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