

## A MODEL FOR RIE OF PZT THIN FILMS

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### Abstract

A simplified model for PZT RIE is presented which describes r.f. discharge kinetics and plasma chemistry in combination with changing surface conditions in gas mixtures of Ar with CF<sub>4</sub> or CHF<sub>3</sub>.

### 1. Introduction

Lead zirconate titanate (PZT) ferroelectric thin films are known for their possible application in nonvolatile random access memories as well as dynamic random access memories. The CMOS integration of ferroelectric materials drives the development of dry etching rather than wet etching techniques of this material. Various techniques of PZT reactive ion etching (RIE) were investigated including different process gases and several plasma sources [1]. Increasing with r.f. or microwave power, the etch rates were obtained, predominantly determined by ion bombardment [2-5], but also with some chemical enhancement as shown by comparison with pure argon sputtering [2,4,6] and a strong substrate temperature dependence [2,7].

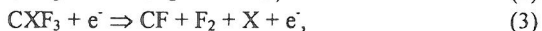
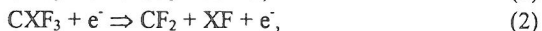
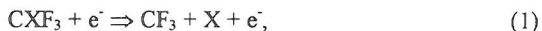
Dry etching process development is usually a series of trial and error experiments. Often a large number of process parameters such as pressure, power, and flow rates and their complex interaction leads to non-optimal process performance. An alternative to this approach is statistical experimental design which determines optimal operating conditions without fundamental understanding. This approach lacks the ability to accurately predict process behaviour outside the experimental parameter space. On the other hand, the effects of ion bombardment on surface modification and surface chemistry are poorly understood. This is manifested by lower etch rates compared to silicon and silicon dioxide [2], unsatisfactory profile angles [3], redeposition of etch products and residue formation [3-5], sidewall roughening [7], a difference in the composition between PZT sidewall surfaces and bulk, and doping of this area by low energy ions such as F and Cl [8], radiation and particle bombardment induced damage influencing the P-E hysteresis, fatigue behaviour and leakage current [9].

In this work, a simplified model for the discharge kinetics and for the plasma and surface chemistry of r.f. discharges containing CF<sub>4</sub>, CHF<sub>3</sub> and Ar gas mixtures for lead zirconate-titanate (PZT) RIE simulation is presented. For a parallel plate deposition reactor with a plug gas flow parallel to the electrode surface, spatially dependent densities of ions and radicals reacting with the electrode and wall surfaces were calculated.

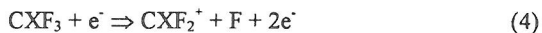
## 2. RIE-simulation model

The RIE-simulation model consists of a discharge kinetics and a plasma chemistry submodel. For discharge kinetics modelling electron-impact rate constants of  $\text{CHF}_3$  were calculated as a function of electron temperature, adopting the electron impact cross sections calculated in [1] and the Maxwellian electron energy distribution function. For  $\text{CF}_4$  cross-sectional values given in [10-13] were employed. The rate constants of Ar were calculated with the electron-impact cross section obtained by [14]. Plasma bulk and sheath parameters were matched considering ions entering the sheath with the Bohm velocity. This simple form of a boundary condition of electronegative low pressure plasmas follows from the existence of almost two different  $\text{CF}_4$  plasmas: an inner positive-negative ion plasma, and an outer electron-positive ion one [13,15]. The density and the temperature of negative ions determine the Bohm velocity of the positive ions entering the sheath, but they have no influence on the dynamics of the positive ions in the sheath. The Bohm velocity in electronegative gases is smaller than in a plasma without negative ions [16]. Calculations were performed considering a nearly collisionless sheath model [17,18].

Considerable knowledge of fluorocarbon low pressure gas discharge interaction with silicon oxide surfaces has been accumulated in literature which may be used in the case of PZT RIE for estimations. Moreover, a mechanism of etching similar to that of  $\text{SiO}_2$  can be expected from similar effects of  $\text{O}_2$  addition on the PZT etch rate [5]. Since an important goal of this work was the development of a computer code for real time decisions in plasma processing, a simplified plasma chemistry model was used. In accordance with calculations in [19] it was assumed that the gas phase chemistry is dominated by a few processes which control the density of  $\text{CF}_3$  and H or F radicals. Electron impact collisions include neutrals formation:



and the generation of the most abundant ion.



where  $\text{X}=\text{F}$  for  $\text{CF}_4$  and  $\text{X}=\text{H}$  for  $\text{CHF}_3$ . The branching ratio for  $\text{CF}_4$  dissociation was taken from [20], that of  $\text{CHF}_3$  was estimated to be 0.64, 0.34 and 0.02 for  $\text{CF}_3$ ,  $\text{CF}_2$  and  $\text{CF}$ , respectively. Due to a lower  $\text{CF}_3\text{-H}$  bond energy (4.6eV) compared to  $\text{CF}_3\text{-F}$  (5.6eV) a higher dissociation degree of  $\text{CHF}_3$  results in the mean electron range up to 10eV [1]. This is valid also for other gases used for PZT-RIE, for instance,  $\text{CF}_2\text{Cl}_2$  [5-7] and  $\text{CHCl}_2\text{CF}_3$  [9]. One consequence of the forced  $\text{CF}_3$  radical generation is an increased concentration of higher fluorocarbons in  $\text{CHF}_3$  compared to  $\text{CF}_4$ .

In a  $\text{CHF}_3$  plasma the fluorine flux toward the substrate is decreased by HF formation [21]. Moreover, for PZT etching the fluorine interaction with the surface is inhibited because of vapour pressures of Pb, Zr and Ti fluorides are too low at temperatures 20-300°C to allow significant vaporisation of these fluorides once they are formed by reactions on the surface [6]. Therefore, the RIE process is probably determined by the reactions of the  $\text{CF}_x$  radicals. A part of the  $\text{CF}_x$  radicals generated by electron impact is lost in the gas phase by recombination with other radicals forming higher fluorocarbons. Since low pressure discharges are operated in the region of the fall-off behaviour of dissociation-recombination reactions [22], the corresponding

reaction rate constants are pressure and temperature dependent. In this work, the recombination rate constants given in [23] were used, which are in good agreement with estimations for  $p = 4$  Pa and  $T = 400$  K.  $\text{CF}_3$  radicals are known to chemisorb on the silicon oxide surface, a process which is enhanced by ion bombardment [24]. The rate constant of the adsorption process  $\text{CF}_3 \Rightarrow \text{CF}_3(\text{s})$  was assumed to be equal to the probability for  $\text{CF}_3$  to collide with the surface

$$k = \sqrt{\frac{RT}{2\pi M_{\text{CF}_3}}} \cdot \exp\left(-\frac{E_{\text{CF}_3}}{RT}\right), \quad (5)$$

where  $R$  is the gas constant,  $M$  the molecular weight and  $E$  the activation energy which was estimated to be 14,7 kJ/mol. Another loss mechanism of  $\text{CF}_3$  radicals in  $\text{CHF}_3$  discharges is hydrogen abstraction:



A similar reaction occurs at the fluorocarbon film surface. In the latter case, the reactive cross section per surface site was assumed to be equal to that in the prototype gas phase reaction. Since collisional deactivation occurs readily at film surfaces, the reaction (6) is then limited by the decomposition of an activated transition state complex with a rate constant independent of pressure. In this case, the main contribution to  $\text{CF}_2$  formation is hydrogen abstraction from the fluorocarbon film surface formed in  $\text{CHF}_3$  discharges due to a higher dissociation degree. The calculated total loss rate of  $\text{CF}_3$  radicals from the gas phase at  $p = 4$  Pa and  $T = 400$  K was  $10^{-11} \text{ cm}^3/\text{s}$ . Reaction eq. (6) also accounts for the higher  $\text{CF}_2$  density in  $\text{CHF}_3$  discharges compared to  $\text{CF}_4$  ones [21].

Ion bombardment effects are primarily responsible for both, high-rate  $\text{SiO}_2$  RIE [25] and PZT-RIE [1]. Ions may remove material from the surface physically (physical sputtering), they may react chemically with the surface to form volatile products (chemical sputtering) or they may promote chemical reactions (ion-enhanced etching).

An important problem for PZT RIE is that  $\text{CF}_x$  radicals should etch all three components of the PZT solid solution –  $\text{PbO}$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$  at reasonable etch rates. Mass spectrometry of volatile species in  $\text{CF}_4/\text{Cl}_2$  high density ECR plasmas shows that fluorine containing radicals are reactive with respect to titania and zirconia [6]. This is confirmed by X-ray photoelectron spectroscopy and Auger electron spectroscopy surface analysis revealing that low pressure  $\text{CF}_4$  plasma selectively removed the Ti-O and Zr-O bonds inducing oxygen vacancies which must be compensated by Ar or Cl admixture selectively breaking relatively weak Pb-O bonds and inducing Pb vacancies by physical sputtering rather than by chemical activity [8]. The described behaviour agrees with thermodynamic estimations, showing that  $\text{PbO}$  with the highest Gibbs free energy is easily converted to  $\text{PbF}_2$ . Thus,  $\text{PbF}_2$  may play a similar part as the thin fluorocarbon film in  $\text{SiO}_2$  RIE. The existence of such a surface layer is confirmed by Pb-containing etch residues [5], a threshold energy of 150 to 200 eV for an effective combination of physical attack and chemical reactivity [6] and a critical power of  $0.2 \text{ W/cm}^2$  for chemical etch rate enhancement in our RIE-system. Usually, a V-shaped PZT etching profile is obtained because of redeposition effects on the sidewalls due to the formation of involatile reaction products and ion induced evaporation at the bottom. The PZT profile angle is increased when decreasing  $\text{CF}_4$  flow, probably limiting fluorocarbon polymer film formation, and when increasing the power of an additional 450 kHz generator used to increase ion energy [3].

Ion bombardment effects were taken into account by the use of surface layer dependent sputter yields. Values for  $\text{Ar}^+$  and  $\text{CHF}_2^+$  ions were estimated from experimental data, for  $\text{CF}_3^+$  the  $\text{CHF}_2^+$  value was used. Fluorocarbon layer free surfaces were described by  $Y_{\text{Ar}^+} = 5 \cdot 10^{-3}$  and  $Y_{\text{CHF}_2^+} = 0.12$ , for fluorocarbon layer coated surfaces the fitted values were  $Y_{\text{Ar}^+} = 9 \cdot 10^{-3}$  and  $Y_{\text{CHF}_2^+} = 1.5 \cdot 10^{-2}$ . The higher values of  $\text{CHF}_2^+$  ions are probably caused by chemical sputtering processes. Since the Bohm velocity in electronegative gases is smaller than in a plasma without negative ions, the ion flux to the substrate is overestimated. Thus, the determined sputter yields are a lower limit.

### 3. Results and Discussion

For a parallel plate deposition reactor with a plug gas flow parallel to the electrode surface, spatially dependent densities of ions and radicals reacting with the electrode and wall surfaces were calculated by solving a set of partial differential equations. Previous, the electron density and the fractions of power dissipation in the plasma bulk, in the sheaths and due to the oscillating sheath boundaries were calculated by the discharge kinetics submodel for given etching parameters. A plasma density of about  $10^{10} \text{ cm}^{-3}$  is predicted at mean electron temperatures of 2.5 to 3.5 eV in agreement with previous models and experiments [13,19,20,21,23,25]. Most of the r.f. power is dissipated by Ohmic heating in the sheath (80 to 85%) and through stochastic heating by the oscillating sheath-plasma boundaries (15% to 20%). The power fraction consumed by the plasma bulk was calculated to be less than 1 %. The calculated ion flux to the substrate has a nearly linear dependence on r.f. power and equals  $5 \cdot 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$  at  $0.5 \text{ W/cm}^2$ .

The PZT etch rate or the deposition rate of fluorocarbon films is given by:

$$R = \frac{M}{\rho \cdot N_A} \left( \sum_i z_i s_i D_i \left. \frac{\partial n_i(x,y)}{\partial y} \right|_{x,y=0} - Y \Phi^+ \right), \quad (7)$$

where  $M$  is the molecular weight and  $\rho$  the density of the deposited or etched material,  $N_A$  is the Avogadro number,  $z_i$  the number of C-atoms in radical  $i$  (deposition) or the reciprocal value of the number of reactive species required to form a volatile product (etching),  $s_i$  the sticking coefficient of  $\text{CF}_x$  radicals taken from [13],  $D_i$  the diffusion coefficient,  $n_i$  the number density of the radical,  $Y$  the sputter yield and  $\Phi^+$  the ion flux to the substrate. The diffusion coefficients for the neutral species were calculated from Lennard-Jones parameters of the intermolecular potential tabulated for different chemical species in [26]. In cases where such data was not available, the diffusion coefficients were estimated using a scaling approach employed for  $\text{Si}_x\text{H}_y$  species in [27].

Etch rates were calculated as a function of r.f. power, total pressure and gas mixture. Due to chemical sputtering, the etch rate in  $\text{CF}_4$  or  $\text{CHF}_3$  is higher than in pure Ar. With increasing argon admixture the thickness of the fluorocarbon surface layer is reduced which in turn causes an increase of the etch rate. At high argon fractions the etch rate is limited by the low  $\text{Ar}^+$  sputter yield attributed to etch residues on the surface.

The gas composition of the transition point between the fluorocarbon layer limited and residue layer limited regimes strongly depends on the reactions constants of the surface reactions. Calculations using the quantum chemistry software GAUSSIAN are in progress now to replace the crude estimates made in this work. High pressure rate constants will be calculated from the

transition state theory (TST) which enables the prediction of rate constants solely in terms of statistical thermodynamic properties of the reactants and the activated complex (transition state). The TST rate constant is:

$$k = \frac{kT}{h} \cdot \frac{Q_i}{\prod_i Q_i} \cdot \exp\left(-\frac{E_A}{kT}\right), \quad (8)$$

where  $Q_i$  and  $Q_i$  represent the partition functions of the activated complex and the reactants determining the entropy change,  $E_A$  is the activation energy, i.e. the difference in energy between the reactants and the activated complex at 0K,  $k$  and  $h$  designate Boltzmann and Planck constants respectively [28]. Rate constants of gas phase reactions determined at high pressure are then linked to their low-pressure values through a two step reaction including (i) energy exchange by collision and (ii) decomposition of the activated complex.

## Conclusions

A simplified model for PZT RIE is presented which describes discharge kinetics and plasma chemistry in combination with changing surface conditions in mixtures of Ar with CF<sub>4</sub> or CHF<sub>3</sub>: physical sputtering in pure argon, surface residue limited etching in mixtures up to about 20 % CF<sub>4</sub> or CHF<sub>3</sub> and a fluorocarbon suppression regime at higher fluorocarbon admixture characterised by an etch rate limited by a thin fluorocarbon film present on the surface. Steep sidewalls and minimum residue formation are expected for gas mixtures just below the fluorocarbon film formation regime.

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