# Sticking coefficient of hydrogen radicals on ArF photoresist estimated by parallel plate structure in conjunction with numerical analysis

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*Abstract*—Investigation of radicals kinetic behavior and estimation of radical sticking coefficient become indispensable for establishing plasma processing control by its internal parameters. This approach is required for plasma processing of single-nanometer gate length field effect transistors and 3diemnsional gates in particular. In our works we have developed new technique for radicals kinetic behavior investigation and its sticking coefficient estimation. Our approach is based on application of parallel plate structure in conjunction with numerical analysis. This approach allows for radicals behavior investigation apart from ions and ultraviolet photons. Moreover this approach allows for analysis role of radical direct and indirect fluxes. By comparison of measured profile thickness and simulated stuck radicals profile we were able to estimate hydrogen radical sticking probability to ArF photoresist.

# I. INTRODUCTION

In the conventional approach, being used nowadays in CMOS main stream manufacturing, the characteristics of plasma processing is adjusted by external parameters such as power, pressure, and gas mixture ratio, which basically depend on the plasma reactor. However, to implement plasma processing on a nanometer scale for future generations of CMOS technology (especially manufacturing 3D FET structures like Multi-gate FET, FinFET), precise control of the plasma is necessary. Etch rate and etched profile shape strictly depend on radical densities (and their ratios) which is strictly related to the radicals sticking coefficients (SCs) [1]. Therefore, internal parameters such as radical densities, energies and their kinetic behavior encompassing SCs must be known, since these parameters directly affect the behavior

of the surface reaction and plasma [2]. In addition to plasma processing the same issue also relates to plasma processing software tools. Although the algorithms for modeling of plasma etching seem to be mature, the capability of quantitative prediction strongly depends on the fundamental physical and chemical data of surface reactions [3]. The most neglected area in this regard is the lack of fundamental data for gas-surface interactions. This in particular concerns to ArF photoresist (PR) because predictive resist modeling remains one of bottlenecks in etching simulation [4]. Chemically amplified ArF resist will remain in CMOS main stream manufacturing for mid-term perspective and it will be used in immersion as well as multiple exposure approaches [6, 1]. Thus accurate models for chemically amplified resists which include surface interactions are needed.

Since *ab-initio* approach to surface interaction requires too heavy computer resources, the experimental validation assisted by computational analysis is not only cost-effective but also indispensable for finding out the principal reaction mechanism.

Investigation of radical kinetic behavior requires development new experimental (and also software) tools and techniques. In our previous studies we have developed techniques for measuring absolute densities of several different radicals and their spatial distributions [1, 2, 5]. In this study we developed technique and investigated the kinetic behavior of hydrogen radicals and estimated its sticking coefficient to ArF photoresist by using parallel plate structure supported by numerical analysis [7].

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# II. EXPERIMENTAL VALIDATION

#### A. Parallel plate structure

In order to investigate the behavior of hydrogen radicals we have used parallel plate structure (Pallet for Plasma Evaluation: PAPE [8], Fig. 1).



Figure 2. Schematic view of PAPE strucrue.

This structure consists of two silicon plates (bottom wafer -BW and parallel plate - PP) coated with 210 nm-thick of ArF photoresist layer (Fig. 2) [9]. Bottom wafer edges are terminated with 0.7 mm-thick silicon walls from three sides. Parallel plate covers 11 mm length of bottom wafer leaving 6 mm uncovered area. Such design of the structure has two purposes. Namely it allows for radical kinetic behavior analysis apart from ions and ultraviolet photons and it also enables for separate analysis of radical direct and indirect fluxes.

#### B. Experiment conditions

In our experiment we have used high-density radical source (HDRS) that uses inductively coupled plasma (ICP) [10] and provides high concentration hydrogen radicals (approximately  $10^{12}$  cm<sup>-3</sup>). Experimental conditions have been shown in Table I.

TABLE I.	EXPERIMENTAL	CONDITIONS

Parameter	Value	
Gas	$H_2$	
Flow rate	100 sccm	
Time	60 min	
RF power	400 W	
Chamber pressure	5.6 Pa	
Substrate temperature	R.T.	

# III. NUMERICAL ANALYSIS

We have performed radical transportation simulations (for the structure shown on the Fig. 2) in order to interpret the role of certain parameters such as PAPE structure geometry and sticking coefficient. We have used Monte Carlo method which has been proved to be correct and useful tool in order to explain measured data for etching as well as for deposition [11, 12]. In our simulation the initial position and incidence angle (between  $-\pi/2$  and  $\pi/2$ ) of each radical are randomly generated on a horizontal *x* axis above the structure.

For low pressures (5.6 Pa in our case) radical free mean path is in order of reactor dimensions, so we assumed collision-less radical movement. The re-emission process is characterized by a single surface reaction coefficient (sticking coefficient) which condenses the complex physic-chemical mechanisms (physisorption, chemisorption, desorption) in a single probability that defines the final attachment of a radical to a surface. The reflection process is continued inside the structure until either the radical adsorbs on the surface (PP or BW) or the radical leaves the structure. It has been proved that single surface reaction coefficient and cosine desorption can properly reproduce the evolution process [11].

# IV. RESULTS AND CONCLUSIONS

After plasma processing of PAPE structure we have performed measurements of PR layer thickness in order to determine its distribution over bottom wafer (Fig. 3) and parallel plate.



Figure 3. 3-dimensional PR thicknes distribution over bottom wafer.

For sticking coefficient estimation we have taken into considerations cross-sectional PR thickness distribution on the bottom wafer (in the center location, Fig. 4).



Practical experiment has been followed by simulation of number of stuck radicals on the bottom wafer (Fig. 5).



In the obtained profiles one can distinguish 3 regions marked on the Figures 4 and 5 as R1-R3. Region R1 is an exposed area (uncovered by parallel plate). In this area 200 nm PR layer has been etched by direct radical flux. Situation is dramatically changed on the region R3 - shadowed by parallel plate where only 30 nm PR layer has been etched (in the point 7 mm which constitutes boundary between R2 and R3). In this area direct radical flux is reduced to zero and etching is done by radicals re-emission. Etched PR profile in this region is not linear and is decaying towards right wall. At the end point (13 mm) etched PR thickness equals 10 nm. In this case re-emitted radicals are being consumed alongside the wafer thus reducing etch rate since there is no direct radicals flux.

Between exposed and shadowed areas approximately 2 mm wide transition region R2 can be observed. This region occurs due to decaying range of influence of direct flux and the presence of re-emitted flux reveals. When sticking coefficient for both wafers was set to 0.2 we have obtained the simulated profile slopes in R2 and R3 ( $\alpha_{R2}$ =76.4°,  $\beta_{R3}$ =3.5° - in assumed

coordinate system PR layer thickness is in accordance with number of stuck radical contributing to the etch process thus we assume that *y* axes on Fig. 4 and Fig. 5 are corresponding) similar to measured ( $\alpha_{R2}$ =74.2°,  $\beta_{R3}$ =3.3°). This value of SC provided also accordance between  $t_{max}/t_{min}$  (Fig. 4) and  $r_{max}/r_{min}$  ratios (Fig. 5) equaling 19 and 19.4 respectively.

Statistics for simulated profile shown on Fig. 5 is presented on Fig 6.



Figure 6. Radicals behavior in PAPE structure.

Simulation exposes that in these conditions approximately 44% out of simulated radicals left PAPE structure after multiple bouncing (11.7% didn't enter PAPE in the first place) while 42% stuck on bottom wafer. For radicals stuck on bottom wafer 78.9% radicals stuck in R1 whereas 16.1% in R2 and 5% in R3 respectively. 8% of total number of radicals simulated reached parallel plate via the re-emission and only 2% radicals took part in etching in this region.

Supplementary simulation revealed that for the experimental PAPE structure length (covered part, 11 mm) to width (structure thickness 0.7 mm) ratio equaling 15.7 radical direct transporting to the right wall in unlike to happen. Only 2.1% out of total number of simulated radicals reached the right wall of the structure directly – without bouncing from bottom wafer or parallel plate. Very small radical incident angle with  $\Delta\alpha$ =7.2° is required. (Fig. 7).



Figure 7. Direct transport radicals incident angle distribution.

Thus re-emission is main radical transport mechanism inside PAPE structure. This assumption can be confirmed by analysis PR etched profile on parallel plate (Fig. 8).



Figure 8. Measured PR profile on PP.

Maximum PR etched thickness is near the plate edge equaling around 30 nm in this point. Due to radicals consumption alongside parallel plate etched PR thickness is decaying towards right wall reaching its minimum value 10 nm (similarly to bottom wafer).

Since there is no direct flux reaching parallel plate, etching on this surface depends not only on its own SC but is also related to SC of the adjacent bottom wafer. Condition on the bottom wafer affects etching characteristics on the parallel plate. Wafer location in relation to the radical source is critical in this regard [15].

In general case the total radical incoming flux on a surface point i can be written as the summation of the direct neutral flux plus all the contributions due to re-emission of the surrounding points j (1, Fig. 9).



Figure 9. Radical transport inside PAPE structure.

# $\Gamma_{radical,i} = \Gamma_{direct,i} + \sum_{j \neq i} (1 - SC_j) g_{ij} \Gamma_{radical,j} \quad (1)$

where:  $\Gamma_{direct,i}$  is the direct flux arriving from the source at the point *i* and  $g_{ij}$  is the form factor that accounts for how much of the re-emitted flux from the point *j* arrives at the point *i*. The form factor depends on the surface geometry and the re-emission (radical bouncing) angular distribution [15].

In our case direct radicals flux is reduced to zero and this part is eliminated from (1). Thus as it has been already stated etching on parallel plate strictly depends on SC of bottom wafer. This also concerns to bottom wafer so it can be stated in general that etch kinetics on the adjacent walls are mutually conjugated. Etching characteristics on one surface depends not only on plasma process internal parameters such as densities and ratios of radicals but also on radical sticking coefficient of adjacent surface.

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