

Development of radical kinetic behaviour investigation method and its application for sticking coefficient estimation

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Abstract—We have developed a new technique for radicals kinetic behavior investigation. Our approach is based on the application of a parallel plate structure in conjunction with numerical analysis. Investigation of radical behavior becomes especially critical for manufacturing devices with single-nanometer gate lengths or devices with 3-dimensional gates in particular. Super-fine etching for such devices requires precisely-controlled plasma processings which can be obtained only by controlling its internal parameters. In this study we present investigation of the sticking coefficient (SC) as the kinetic behavior of hydrogen radical (H^*) in processing of ArF 193-nm photoresist. We primarily obtained 0.2 as the SC of H^* radical on the photoresist using this new technique.

I. INTRODUCTION

In the conventional approach, which is being used nowadays is CMOS main stream manufacturing, the characteristics of plasma processing is adjusted by external parameters such as power, pressure, and gas mixture ratio, which basically depends 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. Therefore, internal parameters such as radical densities, energies and their kinetic behavior encompassing sticking coefficient (SC) must be known, since these parameters directly affect the behavior of the plasma and etch process performance [1].

In order to address these issues in our previous studies, we have developed systems for measuring absolute densities of several different radicals such as hydrogen (H), oxygen (O), nitrogen (N) and carbon (C) based on vacuum ultraviolet absorption spectroscopy (VUVAS) [1-3]. Using our systems we have also successfully measured the spatial distributions of radicals. However, since the radicals in plasma processing

contribute directly to surface reactions, it is also extremely important to understand radical kinetic behavior. This especially concerns to radical sticking coefficient because etch rate and etched profile shape strictly depend on plasma internal parameter namely ratio of radical densities (strictly related to SCs). This parameter must be precisely controlled during processing [3].

On the other hand experimental data obtained in our study are also targeted for modeling and simulation of front-end fabrication process. Although the algorithms for modeling of plasma etching seem to be mature, the capability of quantitative prediction strongly depends on the fundamental physical, chemical data of surface reactions [4]. This especially concerns to ArF resist because predictive resist modeling still remains a bottleneck in etching simulation [5]. Accurate reaction models for chemically amplified resists, which include surface modifications such as line edge roughness, are needed and must be capable of correctly predicting three-dimensional resist patterns.

Thus in this study we have investigated hydrogen (hydrogen-based plasmas are widely used in CMOS technology for etching and in also for deposition) radical kinetic behavior related to surface reactions in ArF photoresist (PR). Our approach is based on the usage of a parallel plate structure supported by numerical analysis [6]. 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.

II. EXPERIMENTAL APPROACH

A. Parallel Plate structure

In order to investigate hydrogen radical kinetic behavior we have used parallel plate structure (PAPE, Fig. 1) [7].

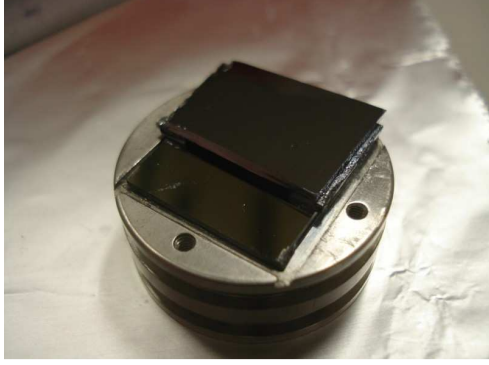


Figure 1. PAPE structure.

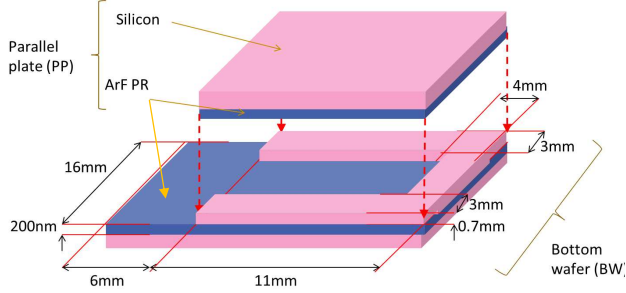


Figure 2. Schematic view of PAPE structure.

PAPE structure consists of two parallel silicon plates (bottom wafer – BW, parallel plate – PP) coated with 200 nm-thick ArF photoresist (Fig. 2) [8]. This kind of structure allows for simultaneous analysis of direct and indirect radical flux and investigation relation between these fluxes separately from ions and ultraviolet photons.

B. Experiment conditions

In our experiment we have used high-density radical source (HDRS) with hydrogen radical concentration approximately 10^{12} cm^{-3} that uses inductively coupled plasma (ICP) [9]. Experiments conditions have been shown in Table I.

TABLE I. EXPERIMENT CONDITIONS.

Parameter	Value
Gas	H ₂
Flow rate	60 sccm
Time	15 min
RF power	400 W
Chamber pressure	5.9 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 [10, 11]. 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 (~ 6 Pa in our case) mean free path of radical 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 [10].

IV. RESULTS AND CONCLUSIONS

A. Radical kinetic behaviour

After plasma processing of PAPE structure we have performed high resolution surface mapping (HRSM) in order to determine PR layer thickness distributions. Three-dimensional PR layer thickness distribution on the bottom wafer and parallel plate after the plasma processing have been shown on Fig. 3 and Fig. 4, respectively.

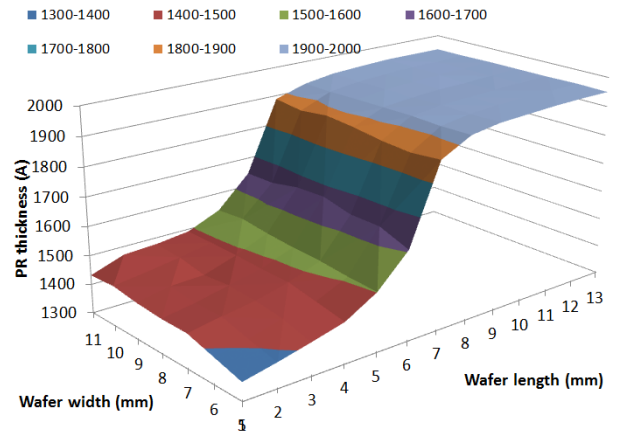


Figure 3. PR thickness distribution over bottom wafer.

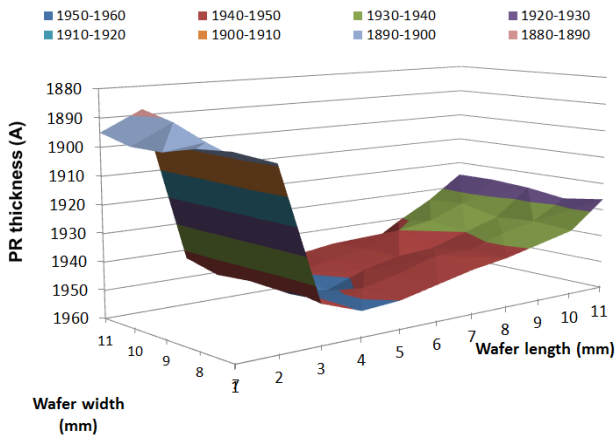


Figure 4. PR thickness distribution over parallel plate.

On the Fig. 5, cross-sectional etched PR profile along bottom wafer length has been shown.

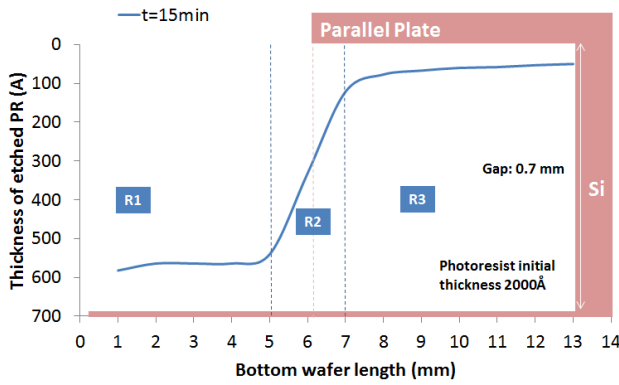


Figure 5. Etched PR thickness cross-sectional profile.

In this profile three different regions marked on the Fig. 5 as R1-R3 can be distinguished. Region R1 is exposed area (uncovered by PP) where nearly 60 nm PR resist has been etched by direct radical flux. Situation is dramatically changed in region R3 – shadowed by parallel plate where only few nanometer PR etching occurred. It stems from fact that in this area direct radical flux is reduced to zero and etching is done only by re-emitted radicals. Etched PR profile in this area is not linear and is decaying towards the right wall. Etched PR thickness equals 12.1 nm for location on bottom wafer at 7 mm (which constitutes boundary between regions R2 and R3) and 5 nm for point 13 mm (right wall location). In this case re-emitted radicals are being consumed alongside the wafer thus reducing etch rate. 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.

B. Numerical analysis

In order to provide better understanding of radical kinetic behavior leading to formation etched PR profile shown on Fig. 5 we have performed calculation of radical stuck profile (Fig. 6) for the structure dimensions shown on the Fig. 2.

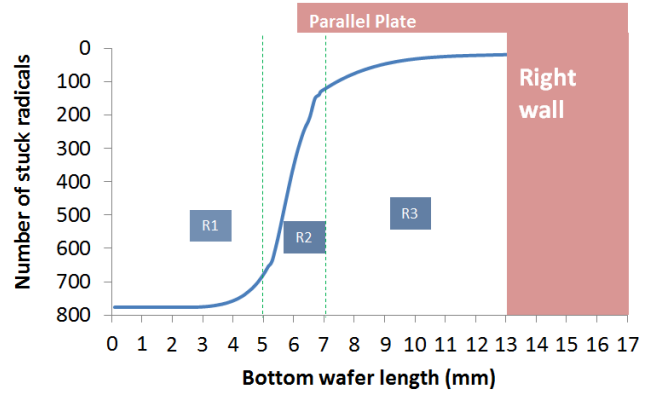


Figure 6. Calculated profile of stuck radicals.

We obtained agreement between etched PR thickness (Fig. 5) and radical stuck profile (Fig. 6) when radical sticking coefficient was set to 0.2. Adjusting SC in order to obtain agreement between shapes of measured etched PR thickness and radical stuck profile on the bottom wafer is our approach to estimate this parameter.

Surface reaction rate constant (etch rate kinetics) is directly proportional to sticking probability (sticking coefficient) and thermal mean velocity of radicals [12, 13]. The total radical incoming flux on a surface point i can be written as the summation of the direct radical flux plus all the contributions due to re-emission of the surrounding points j (EQ. 1, Fig. 7).

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

where: $\Gamma_{direct,i}$ is the direct radical flux arriving from the source at the point i . g_{ij} is the form factor that accounts for how much of the re-emitted radicals 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 (which is assumed isotropic in our case) [14].

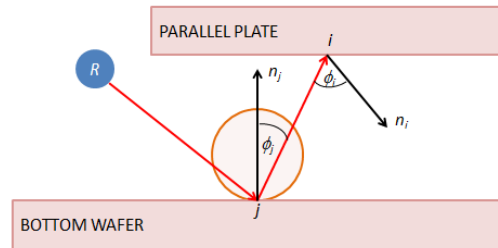


Figure 7. Radical flux mode inside PAPE structure.

Simulation exposes that in these conditions approximately 44% out of simulated radicals left PAPE structure after multiple bouncing. 11.7% radicals didn't enter PAPE – after single bouncing from uncovered by PP part of BW these radicals returned to plasma. 42% radicals stuck on bottom wafer contributing to the etching. 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 (Fig. 7) and only 2% radicals took part in etching in this region (Fig. 4).

We have performed additional simulation investigating radicals entering under parallel plate area (point 6 mm on the bottom wafer). Simulation revealed that for PAPE structure length (11 mm) to width (0.7 mm) ratio which equals in our case 15.7 radicals direct transport to the right wall is 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.

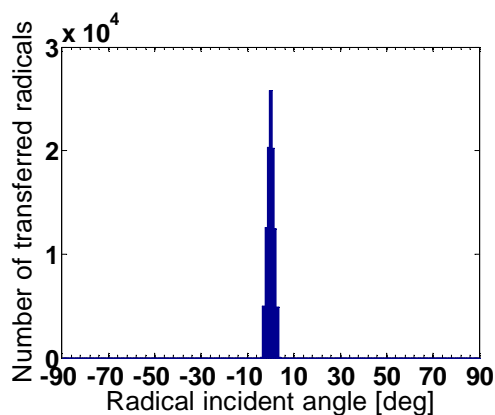


Figure 8. Directly transported radicals incident angle distribution.

For this kind of radical transport to happen very small radical incident angle is required within a range $\Delta\alpha=7^\circ$.

This simulation confirms previously stated conclusion related to etch rate decrease due to radicals consumption alongside bottom wafer and profile decay towards right wall.

Radical kinetic behavior becomes critical factor and it must be understood in order to assure high-performance super fine etching especially 3-dimensional FET structures for future generations of CMOS technology. Proposed in this study method consisting of PAPE structure and numerical tools can help to achieve this goal.

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REFERENCES

- [1] S. Takahashi et al., "Development of atomic radical monitoring probe and its application to spatial distribution measurements of H and O atomic radical densities in radical-based plasma processing", *J. Appl. Phys.* **106**, 053306 (2009).
- [2] W. Takeuchi, H. Sasaki, S. Kato, S. Takashima, M. Hiramatsu and M. Hori, "Development of measurement technique for carbon atoms employing vacuum ultraviolet absorption spectroscopy with a microdischarge hollow-cathode lamp and its application to diagnostics of nanographene sheet material formation plasmas", *J. Appl. Phys.* **105**, 113305 (2009).
- [3] H. Nagai, M. Hiramatsu, M. Hori and T. Goto, "Etching organic low dielectric film in ultrahigh frequency plasma using N_2/H_2 and N_2/NH_3 gases", *J. Appl. Phys.*, Vol. 94, No. 3, 1 August 2003, pp. 1362 – 1367.
- [4] The International Technology Roadmap for Semiconductors: 2009 Edition.
- [5] Sentaurus Topography 3D User Guide, Version E-2010.12, December 2010.
- [6] A. Malinowski et al., "Radical Transport Simulation under Roof on Substrate in Processing Plasma", proc. of 71st Japanese Society of Applied Physics Fall Meeting, September 14-17, 2010, Nagasaki, Japan, DVD-ROM 16a-ZA-7.
- [7] S. Uchida, S. Takashima, M. Hori, M. Fukasawa, K. Ohshima, K. Nagahata, T. Tatsumi, "Evaluation of Property Changes due to Radiation, Radicals, and Ions of Organic Low- k Films in H_2/N_2 Plasma Etching", *Jpn. J. Appl. Phys.* **47** (2008), pp. 3621-3624.
- [8] T. Naito, K. Asakawa, N. Shida, T. Ushiroguchi and M. Nakase, "Highly Transparent Chemically Amplified ArF Excimer Laser Resists by Absorption Band Shift for 193 nm Wavelength", *Jpn. J. Appl. Phys.* Vol. 33 (1994) pp. 7082-7032.
- [9] S. Chen et al., "Behaviours of Absolute Densities of N, H, and NH_3 at Remote Region of High-Density Radical Source Employing N_2-H_2 Mixture Plasmas", *Jpn. J. Appl. Phys.* **50** (2011) 01AE03.S.
- [10] J. C. Rey, L-Y. Cheng, J. P. McVittie and K. C. Saraswat, "Monte Carlo low pressure deposition profile simulations", *J. Vac. Sci. Technol. A* **9**(3) May/June 1991, pp. 1083 – 1087.
- [11] G. Marcos, A. Rhallabi, P. Ranson, "Monte Carlo simulation method for etching of deep trenches in Si by a SF_6/O_2 plasma mixture", *J. Vac. Sci. Technol. A* **21**(1), Jan/Feb 2003., pp. 87 – 95.
- [12] K. Nishioka, M. Sugiyama, M. Nezuka, Y. Shimogaki, Y. Nakano, K. Tada and H. Komiyama, "Optimization of Electron Cyclotron Resonance Reactive Ion Beam Etching Reactors for Dry Etching of GaAs with Cl_2 ", *J. Electrochem. Soc.*, Vol. 144, No. 9, September 1997, pp. 3191 – 3197.
- [13] K. Fujino, Y. Egashira, Y. Shimogaki, and H. Komiyama, "Step-Coverage Simulation for Tetraethoxysilane and Ozone Atmospheric Pressure Chemical Vapor Deposition", *J. Electrochem. Soc.* Vol. 140, No. 8, August 1993, pp. 2309 – 2312.
- [14] J. Li, "Topography Simulation of Intermetal Dielectric Deposition and Interconnection Metal Deposition Processes", Ph.D. thesis, Stanford University, Stanford, CA, USA, March 1996.