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Surface cleaning of small structures during spin rinsing of patterned substrates

Davoud Zamani [a], Kedar Dhane [b], Omid Mahdavi [c], Michael Anthony McBride [a], Jun Yan [d], Farhang Shadman [a,*]

[a] Chemical and Environmental Engineering Department, University of Arizona, Tucson, AZ 85721, USA
[b] Intel Corporation, Chandler, AZ 85226, USA
[c] Micro/Nano Fabrication Center, University of Arizona, Tucson, AZ 85721, USA
[d] Lam Research Corporation, 4400 Cushing Parkway, Fremont, CA 94538, USA

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ABSTRACT

Cleaning and rinsing of small structures are important processes in the manufacturing of micro- and nano-electronics. The latest technology uses “single-wafer spin rinsing” in which ultra-pure water (UPW) is introduced onto the wafer which is mounted on a rotating holder. This is a complex process and its optimization for lowering water and energy usage requires better understanding of the process fundamentals. A mathematical model is presented in this paper that uses the fundamental physical mechanisms and provides a comprehensive process simulator. The model includes fluid flow, electrostatic effects, and bulk and surface interactions. The simulator is applied to the specific case of investigating the dynamics of rinsing of patterned wafers with hafnium-based high-*k* micro- and nano-structures. The effects of key rinse process parameters such as water flow rate, wafer spin rate, water temperatures, wafer sizes, and trench locations in the wafer are studied. Successful incorporation of this rinsing simulator in design and control of surface preparation processes would eliminate dependence on costlier and more time-consuming external analysis techniques.

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1. Introduction

A key step in the sequence of fabrication of semiconductor and other nano-scale devices is the cleaning of the small structures after the substrate, such as silicon or a dielectric layer, is patterned and etched [1]. The cleaning and rinsing of patterned wafers is the most frequently used process, following many other fabrication steps. It is also the single largest user of water in the overall manufacturing process, using over 60% of the water in semiconductor fabrication plants [2]. All modern plants now use equipment that apply spin cleaning and rinsing in which ultra-pure water (UPW) in introduced onto the wafer which is mounted on a rotating holder. Multiple processes, such as desorption and re-adsorption, diffusion, migration and convection, all factor into this rinse process and its potential bottlenecks. Any of these processes can become the rate-limiting step or the bottleneck of the rinse process. Very little is known about the fundamentals of the spin rinsing for patterned wafers. Ensuring optimal resource usage and cycle time during the rinse process requires a sound understanding of the process fundamentals. Additionally, with the advent of new materials such as high-*k* dielectrics, data on the surface interactions is critically needed [3,4].

The fluid flow and mass transfer on rotating disks has been the subject of many studies. For example, Matar et al. [5] have studied the hydrodynamics of thin liquid films flow over spinning disks. They focused on spinning discs operated as continuous flow where the mean properties of the flow are stationary in time. Kaunisto et al. [6] used rotating disk geometry to study the role of mass transfer in the dissolution of the benzoic acid in stagnant liquid. Drumm et al. [7] focused on determining the flow patterns and velocity on rotating wafers using particle image velocimetry. The focus of these examples and other previous work has been on the fluid flow and mass transfer in the fluid film above the rotating disk. This aspect of rotating disk system, while important, is not the objective or the focus of the present study.

The problem that is being studied here is the mechanism of cleaning of nano-structures that exist in a rotating patterned wafer. Patterned wafers are not plane disks and the bottleneck of their cleaning is not the fluid flow and mass transfer in the fluid layer above the disk and on their top surface. The process that is the focus of this work includes the transport of impurities out of the high-aspect-ratio (deep) nano- and micro-structures that have been etched in these wafers by the patterning process. The fluid mechanics and mass transfer in the layer on the top of the rotating

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* Corresponding author. Tel.: +1 520 621 6052; fax: +1 520 626 5397.
E-mail address: shadman@erc.arizona.edu (F. Shadman).

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Nomenclature

C_i	concentration of ion *i*
C_s	surface concentration
D_i	diffusivity of ion *i*
D_F^-	diffusivity of fluoride
D_H^+	diffusivity of proton
D_{OH}^-	diffusivity of hydroxide
e	charge of an electron
ECRS	electro Chemical Residue Sensor
F	Faraday constant
F^-	fluoride ion
H	water film thickness
HF	hydrofluoric acid
H^+	proton ion
IEP	isoelectric point
k_a	adsorption rate coefficient
k_d	desorption rate coefficient
K_w	dissociation constant of water
N	normal vector
N_i	flux of ion *i*
OH^-	hydroxide ion
Q	volumetric flow rate
QCM	quartz Crystal Microbalance
R	gas constant
r	radius
S_0	maximum available site
t	time
T	temperature
u	velocity
UPW	ultra-pure water
u_r	velocity in *r* direction
u_z	velocity in *z* direction
z_i	valence of ion *i*
ε	dielectric constant
κ_B	Boltzmann constant
μ_i	ionic mobility of ion *i*
ν	kinematic viscosity
ρ	spatial charge density
σ	surface charge density
φ	electric potential
ω	angular velocity

disk is integrated with the detailed equations of transport, electric field, surface charge and surface adsorption/desorption processes that occur inside these structures. These aspects, critical in dealing with patterned wafers, have not been studied so far. The other aspects of the process not investigated are the critical effect of electric field, generated due to surface charge, on the mass transfer inside the micro- and nano-structures and the dynamics of this transient process, since the rinse process is inherently at unsteady state condition.

The specific case selected for this study is the removal of residual HF from hafnium oxide substrate. This combination is very relevant to the latest widespread use of hafnium-based dielectrics in semiconductor manufacturing. The interactions parameters found by using these test materials will be very valuable for researchers working on high-*k* processing. In our prior studies [3,4], we have reported the interactions parameters of HF with hafnium oxide. The method of approach and the process simulation results in the present work are applicable to all substrate and impurities. Moreover, the application of the results is not limited to semiconductor manufacturing but to fabrication of other nano-structures used in optoelectronics and microfluidic components.

2. Method of approach

The present work focuses on the development of a comprehensive rinse model that takes into account the ionization of typical impurities, the surface interactions such as adsorption/desorption, and the electric field impact on the transport of ions. The electric field is generated by the surface charge due to the fluid surface interactions. Based on this process simulation, the role of different parameters, including spin rate, flow rate, temperature of water, wafer size, and feature size, is investigated in single-wafer cleaning tools.

An Electro-Chemical Residue Sensor (ECRS) was used for obtaining the temporal concentration profile of chemical residues inside micro-structures during the rinse process. The sensor provides excellent sensitivity and is capable of in situ and real-time monitoring of the cleaning process in the single-wafer cleaning tools. The ECRS metrology method as well as the formulation of the processes that take place in the trench is reported elsewhere [8,9].

3. Overall process description

The schematic of the fluid flow pattern on the surface of a spinning wafer during the rinse process is shown in Fig. 1a. The rinse water introduced at the center of the wafer flows over the surface of the wafer from the center towards the edge. The shape of the water film is symmetric around the *z* axis. The trench, shown in Fig. 1b, represents a micro- or nano-structure. The rinse water layer on the wafer consists of two regions: (1) inside the trench features to be cleaned, and (2) inside the film formed on the spinning wafer.

The individual steps involved in the impurity rinse and removal process are affected by the surface charge on the walls of the substrate which is affected by the composition in the boundary layer near the wafer surface. The key configuration and operating parameters involved in the development of the process model for single-wafer spin rinsing tools are speed of rotation, water flow rate, water temperature, wafer size, feature size, and the initial contaminant concentration. The contaminant in this study is 1% hydrofluoric acid. The model takes into account the details of the rinse process including chemical reactions in the liquid phase and on the hafnium based high-*k* surfaces, as well as the diffusion, convection, and migration under the electric field. The model parameters, such as surface interaction rate coefficients and diffusivity, depend on the type of impurity and the chemical nature of the surface.

Impurity chemicals are initially on the wafer and also inside the trench, both in the bulk and on the surface. When wafers are exposed to the rinse water, the chemical contaminants dissolve in the rinse water and are converted to their ionic form due to dissociation [10]. The model contaminant in this study is 1% hydrofluoric acid. The following reactions represent the dissociation of HF in rinse water.

$$HF \overset{K_1}{\leftrightarrow} H^+ + F^-, \quad K_1 = 0.685\,\text{mole/m}^3 \tag{1}$$

$$HF + F^- \overset{K_2}{\leftrightarrow} HF_2^-, \quad K_2 = 0.03963\,\text{m}^3/\text{mole} \tag{2}$$

$$2HF \overset{K_3}{\leftrightarrow} H_2F_2, \quad K_3 = 0.0027\,\text{m}^3/\text{mole} \tag{3}$$

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