Thermal Effects of SPM Solution for Polished SiO_2 film and Adsorbed Ceria Nano-particles on Single Wafer Cleaning

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INTRODUCTION

Caria nanoparticles which have been used to remove SiO_2 film rapidly and selectively form Ce-O-Si bonds with proposed chemical reaction (-Ce-OH + -Si-O^- ↔ Ce-O-Si^- + OH^-) on the SiO_2 film surface when polishing swallow trench isolation (STI) and inter layer dielectrics (ILDs). Adsorbed ceria nanoparticles with Ce-O-Si bonds are hard to remove from the SiO_2 film surface than other residues and harder to remove smaller sized ceria nanoparticles than before.[1]

For the effective removing of residual ceria nanoparticles on the SiO_2 film surface, Seo et al. optimized the mixture ratio of ammonium hydroxide (30wt% NH_4OH) and hydrogen peroxide (30 wt% H_2O_2) solutions to maximize the concentrations of perhydroxyl ions (HO_2^-) as an break the Si-O bond.[2] Further, Gowda et al. developed cleaning solutions with chemical additives as the prohibition for re-adhesion of detached ceria nanoparticles from the both SiO_2 and Si_3N_4 film surface.[3]

Moreover, the mixed solution of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) which called SPM or piranha solution is significantly concerned and used to cleaning process for semiconductor device manufacturing due to its effects for not only removing organic residues but also the cleaning of ceria nanoparticles with strong oxidizing agent after chemical mechanical planarization (CMP).[4] Especially, single wafer cleaning method using SPM under directly mixing of chemicals in the spray nozzle increasingly applied in practical cleaning process.

Even though SPM single cleaning method qualified, study for thermodynamics of SPM solution and correlation of cleaning effect is not sufficiently studied before. In this reason, temperature of SPM has been expected while H_2SO_4 and H_2O_2 solutions are supplied to the spray nozzle with various flow rate. And behaviors of fluid are expected while SPM is sprayed on the SiO_2 deposited wafer. Also, for the verification experiments, experimental set-up and related results will be described.

BACKGROUND

For the thermodynamical expectation of $H_2SO_{4(aq)}$ and $H_2O_{2(aq)}$ mixture in the spray nozzle, The Navier-Stokes equations are used to describe both the chemical reaction process and the cleaning process and discretized with the Finite Volume Method (FVM). The Navier-Stokes equations can be generally described as the follow format based on various transported scalar.

$$\frac{\partial \rho \phi}{\partial t} + \nabla \cdot (\rho \phi U) = \nabla \cdot (\mu \nabla \phi) + S_\phi \tag{1}$$

The probability density function (PDF) and volume of fluid (VOF) model are used for descriptions of chemical reaction and solution interface capture, respectively where the mixture fraction and the volume fraction of solution are transported. The expression for mean scalar value based on probability and mixture fraction are as follow [5,6].

$$\overline{\phi_t} = \int_0^1 P(f) \mu \phi_i(f) df \tag{2}$$

$$f = \frac{Z_i - Z_{i,ox}}{Z_{i,fuel} - Z_{i,ox}} \quad (3)$$

The Lee model was used to describe the mass interaction between phases, while for the description of the solution heat of sulfuric acid, a conservation regime of chemical energy is introduced here and appended as a source term inside the energy equation which can be described as follow. The commercial platform ANSYS FLUENT was used combined with user defined function (UDF) for this work.

$$\sum_{C}\sum_{F} energyperface + \frac{\partial}{\partial t}\rho C_{H_2SO_4} \cdot Volume \cdot \varphi\left(C_{H_2SO_4}\right) = \nabla \cdot \Gamma \cdot grad\phi + source \quad (4)$$

EXPERIMENTAL

For the verification of simulation results, experimental apparatuses are preparing like depicted in Fig. 1. Sulfuric acid and hydrogen peroxide solutions will be supplied to the SPM spray nozzle and quantitatively controlled by syringe pump. Two temperature sensors will be placed to inside and outlet of SPM spray nozzle. Also, thermal imaging camera will be placed to observing sprayed SPM solution on the surface of wafer. Monitored temperature values will be correlated with simulation results as an verification methods.

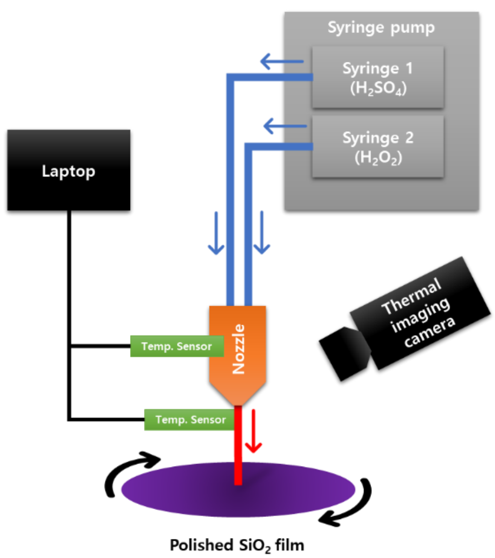

Fig.1 Experimental set-up for verifying expectation of sulfuric acid and hydrogen peroxide reactions and cleaning efficiencies for ceria nanoparticles on the polished SiO_2

DISCUSSION

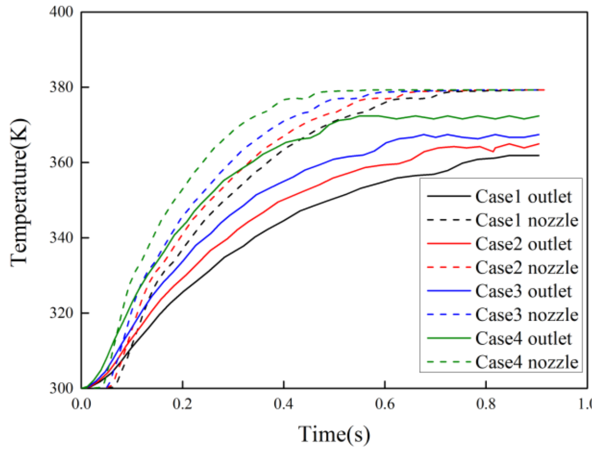

Fig.2 Average temperature development at outlet and in whole SPM spray nozzle

The case1 – case 4 refer to flow ratio between sulfuric acid (99wt% H_2SO_4) and hydrogen peroxide (30wt% H_2O_2) as 3:1, 3.5:1, 4:1 and 5:1 respectively. The tendency in the reaction process is shown based on the simulation results that the temperature increases fast and stays stable, which can be explained by the thermal effects of sulfuric acid dilution process, the main factor for the temperature change in this process, as well as the phase change triggered by the severe exothermic process. As the flow rate of the sulfuric acid increase, the settling time decreases, while the average temperature at outlet increases.

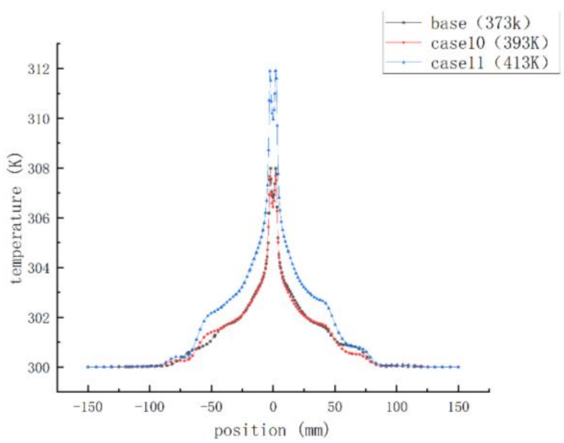

Fig.3 Temperature distributions of SPM solution according to temperature 373 K (black), 393 K (red), and 413 K (blue), respectively

For the cleaning process, the thickness uniformity of SPM solution has correlation with the rotation speed which can be explained by the introduction of the stronger centrifugal force. The temperature distribution closely depends on the flow rate and the temperature of the mixed solution. The temperature distribution on the wafer surface follows the same tendency as the thickness of the thin film of the solution, which can be explained by the heat conduction between the wafer and the solution of high temperature. Apart from the mass of fluid transported, the influence of flow rate probably also comes from the intensity of the turbulence which will be studied in the future works.

CONCLUSIONS

The numerical model for chemical reaction of sulfuric acid (99wt% H2SO4) and hydrogen peroxide (30wt% H_2O_2) in the SPM spray nozzle and fluid dynamic of sprayed SPM on the SiO_2 film wafer are established and discretized with FVM. The mixture ratio has major influence on the thermal effects of the sulfuric acid and hydrogen peroxide mixed solution and uniformity of the SPM solution has difference with flow rate of sprayed SPM solutions, which are convinced to account for the factors for the efficiency of the cleaning process. Also, experimental verifications will be correlate with the simulation results.

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