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Study of interaction between silicon surfaces in dilute ammonia peroxide mixtures (APM) and their components using atomic force microscope (AFM)

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ABSTRACT

Force measurements have been conducted between H-terminated Si surface and Si tip in DI-water, $NH_4OH:H_2O$ (1:100), $H_2O_2:H_2O$ (1:100) and $NH_4OH:H_2O_2:H_2O$ (1:1:100–1:1:500) solutions as a function of immersion time using atomic force microscopy (AFM). The approach force curve results show attractive forces in DI-water, $NH_4OH:H_2O$ (1:100) and $H_2O_2:H_2O$ (1:100) solutions at separation distances of less than 10 nm for all immersion times (2, 10 and 60 min) investigated in this study. In the case of dilute ammonia–hydrogen peroxide mixtures, the interaction forces are purely repulsive within 2 min of immersion time.

The adhesion forces have also been measured between the surface and the tip in DI-water, $NH_4OH:H_2O$ (1:100) and $H_2O_2:H_2O$ (1:100) solutions. The magnitude of the adhesion force is in the range of 0.8–10.5 nN in these solutions. In dilute APM solutions, no adhesion force is measured between the surface and the tip and repulsive forces dominated at all separation distances.

1. Introduction

With continuous shrinking of semiconductor devices, removal of submicron particles and organic contaminants from silicon wafers has become critical for improved yield and proper functioning of devices [1]. Wafer cleaning is a critical step in device fabrication and it is estimated that over 50% of the yield loss in semiconductor manufacturing is due to micro-contamination [2,3]. Not only is the number of cleaning steps increasing but also more stringent requirements are being imposed by the International Technology Roadmap for Semiconductor (ITRS). For 32 nm technology node devices, the ITRS requires the critical particle diameter and count to be 17.9 nm and 113.3 #/wafer, respectively, for the front surface of a 300 mm wafer [4].

One of the most widely used wet cleaning chemical systems for particle removal in semiconductor manufacturing is a mixture of ammonium hydroxide (NH_4OH), hydrogen peroxide (H_2O_2) and de-ionized water (DIW) known as APM or SC-1 solution. The conventional APM mixture consists of NH_4OH (29%), H_2O_2 (30%) and DI-water in the ratio of 1:1:5 and is typically employed at ~70–80 °C with or without megasonic energy [5]. Particle removal from silicon wafer surfaces in APM solutions has been widely studied and well documented [6–8]. The cleaning mechanism is based on oxidation of hydrophobic Si surface by H_2O_2 followed by the etching of silicon dioxide by NH_4OH. Additionally, APM solution provides a condition under which dislodged particles and surface experience electrostatic repulsion which prevents re-deposition of particles onto the surface.

One of the disadvantages of using a 1:1:5 APM solutions for cleaning is that it etches silicon at a rate of 0.3 nm/min at 80 °C [9]. With the shrinking of technology node to 32 nm and lower, such etch rates have become unacceptable. The ITRS dictates that the loss of silicon be less than 0.3 Å per cleaning step for 32 nm technology nodes [4]. This has generated interest in the use of dilute APM solutions. Currently, the dilution level is optimized based on particle removal efficiency data [10,11]. An alternative approach to choose an optimal APM ratio is through a systematic study of interaction forces between particles and surfaces.

Interaction forces between surfaces can be measured using the surface force apparatus (SFA) [12,13] and the atomic force microscope (AFM) [14–16]. In particular, AFM has emerged as a powerful tool for measuring interaction forces between two surfaces in vacuum, air and liquid media. The principle of AFM surface force measurements is well described in literature [17–19].

Several authors have published AFM studies relevant to semiconductor processing [20–23]. One such study reports interaction force measurements between a silicon nitride tip and hydrophobic silicon surface in DI-water and 0.5 wt.% HF solution at a pH of 1.88 [21]. Electrostatic repulsive force was measured starting at a

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separation distance of ~40 nm in DI-water. At distances less than 10 nm, the force becomes attractive. In HF solution, the interaction force was attractive at all separation distances. In another published study, interaction force measurements were conducted between a hydrophilic SiO_2 particle (5 μm) and a hydrophilic SiO_2 surface in DI water [22]. A purely repulsive force starting at a separation distance of ~40 nm due to interaction of double layers formed on negatively charged oxide surfaces was measured.

AFM technique can also be used to measure adhesion forces between particles and substrates [24–26]. For example, adhesion forces between a polystyrene sphere (5 μm) and a SiO_2 surface in 0.03 M KNO_3 solution in the pH range from 2 to 10 have been reported [27]. The results show a strong dependence of adhesion forces on pH. For solutions at pH values lower than 4.0, a strong adhesion force of 127 nN was measured. The decrease in adhesion force at alkaline pH solutions was attributed to high silicon surface roughness caused by etching. Same authors have also reported the measured adhesion forces between alumina particles and silicon dioxide surface in DI-water, 0.2 wt.% NH_4OH and 0.2 wt.% H_2O_2 solutions [28]. The measured adhesion forces in NH_4OH and H_2O_2 solutions are ~2.5 times higher than that in DI-water. This effect was attributed to the change in the surface chemistry of alumina particle in solutions of different pH. In another publication, adhesion force between silica particles and copper surface in different cleaning solutions of relevance to post-CMP cleaning has been reported [29]. In citric acid solution containing tetramethyl ammonium hydroxide (TMAH), adhesion force of 9 nN was measured, whereas a replacement of TMAH with NH_4OH lowered the adhesion force to 0.012 nN. It was concluded that the appropriate selection of the pH and the chemical additives are important in the control of adhesion force between particle and surface.

In general, the measured adhesion force between a particle (or AFM tip if used to simulate a particle) and a substrate in a wet cleaning scenario is mainly due to van der Waals force [30–33], which is given by Eq. (1)

$$F_{\mathrm{vdW}} = -\frac{A_{\mathrm{H}}R_{\mathrm{T}}}{6D^2} \tag{1}$$

In this equation, A_{H} is the effective Hamaker constant between the particle and surface in a particular medium, R_{T} is the radius of the particle or AFM tip and D is the closest separation distance between the particle and the substrate. For a system where the precise value of the A_{H} is not known, AFM has been employed to calculate the A_{H} from adhesion force during the retraction of particle from the surface [16,31]. An alternative method uses the experimentally measured jump-in distance between the tip and the surface during the approach of particle towards surface to calculate A_{H} [16]. The tip jump onto the surface occurs when the force gradient exceeds the spring constant (k_s) of the cantilever as shown in Eq. (2)

$$\frac{dF}{dD} \geqslant k_s \tag{2}$$

The total force of interaction between a surface and a tip would typically consist of attractive and repulsive components. In systems where repulsive forces are due to electrical double layer (EDL) interaction and the attractive force is mainly due to van der Waals (vdW) interaction force. The total interaction force, F_{tot}, may be expressed as follows:

$$F = k_1 \exp(-k_2 D) - \frac{A_{\mathrm{H}}R_{\mathrm{T}}}{6D^2} \tag{3}$$

The first term in this equation represents EDL interaction force, and the second term is the attractive vdW force. The electrical double layer interaction force, which has an exponential relation to distance, can be calculated if zeta potential of interacting surfaces is known. Alternatively, based on the work of Israelachivili and Adams [34], repulsive forces can be calculated by fitting an exponential function of the type $k_1 \exp(-k_2 D)$ to data points in the range of 5–60 nm, where k_1 and k_2 are fitting constants. By differentiating Eq. (3) with respect to separation distance (D) and equating to the cantilever spring constant (k_s), A_{H} can be calculated as shown in Eq. (4)

$$A_{\mathrm{H}} = \frac{[k_s + k_1 k_2 \exp(-k_2 D_{\text{jump-in}})]\,3D^3_{\text{jump-in}}}{R_{\mathrm{T}}} \tag{4}$$

In the case where only attractive forces are present between a surface and a particle, A_{H} values can be calculated using van der Waals interaction force as shown in Eq. (5)

$$A_{\mathrm{H}} = \frac{3(D_{\text{jump-in}})^3 k_s}{R_{\mathrm{T}}} \tag{5}$$

Published Hamaker constant values for different materials using equations [1] or [4] are in reasonable agreement [35–37].

The purpose of this study is to investigate the interaction forces between a silicon surface and a silicon tip in various solutions that include DI-water, NH_4OH:H_2O (1:100), H_2O_2:H_2O (1:100) and NH_4OH:H_2O_2:H_2O (1:1:100) using atomic force microscopy (AFM). The tip has been used to simulate small particle in the context of semiconductor wafer cleaning.

2. Experimental procedures

2.1. Materials

Si(1 0 0) samples (p-type, 38–50 Ω-cm) were used for force measurements. De-ionized water (18 MΩ-cm) was used to prepare all the experimental solutions. Ammonium hydroxide (29 wt.%), hydrogen peroxide (30 wt.%), and hydrofluoric acid (49 wt.%) of electronic grade were purchased by Ashland Chemicals. Silicon nitride cantilevers (SNL-10, Veeco Instruments, CA, spring constant of 0.12 N m^{-1}) with a silicon tip were used in this study.

2.2. Surface preparation

Si wafers were diced into 1 × 1 cm^2 pieces and cleaned by sonicating in acetone and methanol for 5 min, respectively. Samples were rinsed with DI-water and blown dry with ultra-pure N_2 gas. H-terminated Si surface was prepared through the removal of native oxide layer in a mixture of hydrofluoric acid and DI-water at a volume ratio of 1:100. Finally, the samples were rinsed thoroughly with DI-water and dried with ultra-pure N_2 gas. A freshly prepared Si sample was used for all experiments. Silicon tips were prepared using the same method as that for silicon wafers.

2.3. Contact angle measurements

Contact angle measurements were conducted with a goniometer (Reme-Hart Instrument Company, Mountain Lakes, NJ) using the sessile drop method. HF treated silicon samples were immersed in DI-water, NH_4OH:H_2O (1:100), H_2O_2:H_2O (1:100) and dilute NH_4OH:H_2O_2:H_2O solutions for 2, 10 and 60 min, followed by rinse with DI-water and blown dry with N_2 gas. Several drops of liquid (0.25 μL) were placed on the sample and the average values are reported.

2.4. Surface force measurements

Surface forces were measured using a Digital Instrument Nanoscope IIIa atomic force microscope (Veeco Instruments, CA). A sealed liquid cell (volume less than 0.2 mL) was used for the measurements which were carried out at room temperature (24 ± 1 °C).