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Chemical effects on the tribological behavior during copper chemical mechanical planarization

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HIGHLIGHTS

- Chemical roles of friction as functions of slurry pH during CMP are investigated.
- The formation of Cu-BTA complex under acidic conditions increased COF.
- Chemical dissolution under alkaline conditions resulted in lower COF.

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ABSTRACT

Copper chemical mechanical polishing/planarization (CMP) is subject to mechanical actions by abrasive wear coupled with simultaneous chemical effects via slurries at the wafer/pad interface. Therefore, it is necessary to investigate slurry chemical effects on the contact interface. The chemical roles of friction as functions of slurry pH during copper CMP process were studied. The wettability and particle size of the slurry had non-dominant influence on the friction force of the polishing interface. According to OCP measurements, XPS and Raman analysis, chemical reactions occurring on the polishing interface led to varying the tribology behavior during CMP process. The formation of Cu-BTA complex under acidic conditions increased the coefficients of friction (COF), while chemical dissolution under alkaline conditions resulted in lower COF. The results provide more understanding of tribological principles and further optimization of the CMP process.

1. Introduction

Chemical mechanical polishing/planarization (CMP) has emerged as one key process step to planarize copper dual damascene structures in integrated circuit (IC) manufacturing. However, as the scale of features shrinks and low-k and ultralow-k materials are introduced into interconnect structures, conventional CMP faces many technical challenges. For example, low-*k* materials are mechanically weak and contain high levels of porosity, which may be damaged by mechanical energy of the contact interface (i.e., friction) during CMP process. Besides, the frictional force generated during CMP processes has significant effects on the polishing performance as it directly impacts the pad surface temperature and material removal rate [1]. Therefore, it is critical to investigate the tribological fundamentals of copper CMP.

There have been a number of studies available in literature on the tribological behaviors of copper during CMP, such as friction force, lubrication mechanism, abrasive adhesion phenomena, etc [2–7]. Levert [5] investigated the coefficient of friction of SiO_2 substrate on a polyurethane CMP pad as a function of the slurry's SiO_2 abrasive particle concentration and size with a commercial pin on disk tribometer. Liang [6] considered CMP functions similar to chemical boundary lubrication of mechanical systems, resulted from chemical interactions between chemical compounds in liquid lubricants and the solid sliding surfaces. Fu [8] evaluated the coefficient of friction (COF) and wear rate for the material removal mechanism by the combination of surface plowing and shearing under a single-particle scratch. Besides, the rheological behavior of slurry is an important parameter that can influence the slurry film thickness between the pad and wafer, and affect the friction at the pad-abrasive-wafer interface; furthermore, alter the material removal rate during CMP process. Zhao [9,10] studied the interfacial fluid behavior during the polishing process of 12-inch silicon wafer

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and its basic mechanical polishing variables. For commercially available colloidal and fumed silica CMP slurries containing about 30% abrasives, it was found the CMP slurries behaved as Newtonian fluids with nearly constant viscosities at low shear rates (100–10,000 s^{-1}), while the slurry displayed shear thickening behavior upon increasing the shear rate [11,12]. Besides, the suspending media, such as DI water and 0.5 M KCl solution, both behaved as Newtonian fluids [11]. Thus the colloidal silica plays a dominant role in the shear thickening behavior. From Zhao's study [13], slurry pH changes only slightly altered the slurry apparent viscosity. Especially at low concentration of abrasives, the slurry exhibited a fairly constant and low viscosity across the entire pH range [14].

Therefore, the tribological behaviors due to mechanical and physical factors have been studied deeply. Since copper CMP process involves both mechanical actions and chemical effects, it is necessary to investigate slurry chemical effects on the tribological principles of CMP processes. Therefore, in this work, the studies focus on the chemical factors of friction as functions of slurry pH during copper CMP process. The results are benefit for further optimizing the slurry and operating conditions, to avoid structural damage during future CMP process.

2. Experimental

2.1. Components and physical properties of slurries

CMP slurries were prepared with deionized water and reagent grade chemicals which were purchased from Sinopharm Chemical Reagent Co, Ltd. (SCRC). The basic slurries solution contained 3 wt% hydrogen peroxide (H_2O_2), 1 wt% glycine ($C_2H_5NO_2$), and 0.05 wt% benzotriazole (BTA, $C_6H_4N_3H$), in which H_2O_2 served as the oxidizing agent, glycine as the complexing agent and BTA as the inhibitor. To study the effect of pH value on the removal mechanisms of copper, the pH ranges of slurry were adjusted by sulfuric acid (H_2SO_4) and potassium hydroxide (KOH) from 4 to 10. The wettability of slurries on Cu was obtained by taking photographs immediately after dropping 2 μL of the solution onto a fresh Cu surface. In chemical mechanical polishing experiments, colloidal silica with the average diameter of 25 nm was added to the basic slurries at a concentration of 3 wt%. The zeta potential of the particle surface was tested by Zetasizer Nano (Malvern Instruments).

2.2. Chemical mechanical polishing

Chemical mechanical polishing experiments were performed using a CETR CP-4 bench-top polishing tester with 2 in blanket copper wafers (copper deposited on a silicon wafer with tantalum as a bonding layer). The CMP pad used IC1010/Sub-IV composite pad (Dow Electronic Materials, USA), with the slurry pumped on to the pad at a flow rate of 100 ml/min. The platen and wafer were rotated at 150r/min with an applied force of 3Psi. Weight changes after polishing were measured by an electron analytical balance (Sartorius ME235S, ±0.01 mg) to calculate the material removal rate of copper. The removal rate was the average of six individual polishing experiments. The coefficients of friction (COF) during the planarization process were measured in situ. A two dimensional force sensor is used to measure the lateral force between the wafer and pad as well as measuring and controlling the loading (vertical) force during CMP process. The COF (μ), defined as the ratio of the lateral forces (parallel to the planarization interface, the F_x and F_y components) to the vertical forces (perpendicular to the interface, the F_z component), can be given as

$$\mu = \frac{\sqrt{F_x^2 + F_y^2}}{F_z} \quad (1)$$

2.3. Open circuit potential (OCP) measurements

The OCP experiments were carried out with a 273A EG&G potentiostat (Princeton Applied Research) in a three electrode electrochemical cell. A saturated calomel reference electrode (SCE) and a platinum counter electrode were used. The working electrode was a pure copper cylinder (99.9 wt%) with the diameter of 5 mm encased in epoxy resin. Prior to each experiment, the cross section of the electrode, used as working surface, was freshly abraded with abrasive SiC paper grit 2000, then carefully degreased with absolute ethanol and dipped in dilute H_2SO_4 to remove any naturally oxidized species from the copper surface.

2.4. Surface analysis

To investigate the chemical reactions of the copper surface, PHI Quantera SXM X-ray photoelectron spectroscopy (XPS) system and Raman spectra were introduced. After some time of immersion in the basic slurries solution, the copper specimens were rinsed with DI water, dried by N_2, and sealed in vacuum before XPS and Raman analysis. During XPS analysis, the anode target is Al, the energy resolution is 0.5 eV and the vacuum of the analysis chamber is 6.7×10^{-8} Pa. Raman spectra were measured using a Horiba Jobin Yvon Raman spectrometer. A HeNe laser (632.8 nm) with a power of about 1 mW was projected onto the surface of the wear track. Such low intensity is unlikely to alter the copper surface and oxide films during measurements. Collection time was of 1 min with 2 times accumulations for each spectrum. Calibration was done referring to the 520.7 line of silicon.

3. Results and discussions

3.1. COF analysis

During the CMP process, the friction usually could be occurred between the surfaces of pad, abrasives, and wafer, which depended on the roughness, texture, mechanical and chemical properties of the surface [15,16]. The coefficients of friction (COF) during the

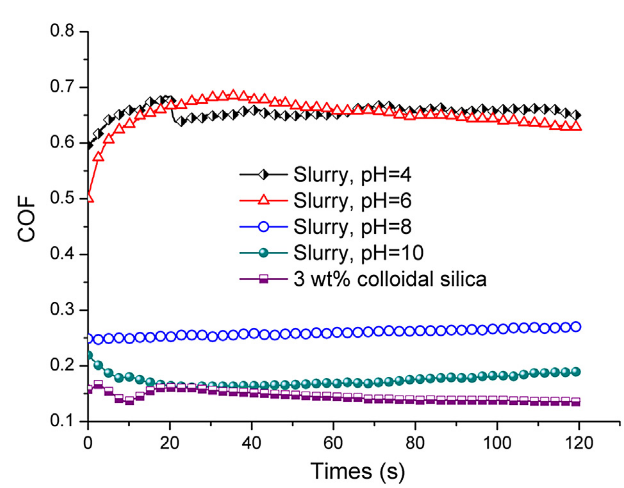

Fig. 1. Friction coefficients over time during CMP process.