



Effects of physico-chemical properties between poly(ethyleneimine) and silica abrasive on copper chemical mechanical planarization



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ABSTRACT

We investigated the effect of poly(ethyleneimine) (PEI)-modified silica abrasive on the removal rate and the degree of dishing during Cu chemical mechanical planarization (CMP). The PEI-modified silica abrasive was prepared by mutually attractive electrostatic forces between PEI and silica abrasive. The physico-chemical behaviors between PEI and the silica abrasive were evaluated by total organic carbon (TOC), force-separation measurements using atomic force microscopy (AFM) with molecular weight of PEI, which was found to adsorb on silica at pH 7.0 following a Langmuir isotherm. The maximum adsorbed amounts of low and high molecular weight PEI were 0.195 mg/m² and 0.228 mg/m², respectively. AFM results showed the repulsive force of the adsorbed PEI layers on the silica surface and the adsorption thickness of PEI on silica vary with the molecular weight of PEI. A twofold change was observed in the AFM analysis. First, the increased areal density of adsorbed PEI caused a higher zeta-potential and longer reaching repulsive force. Second, the adsorption thickness was also significantly enlarged. High molecular weight showed increased adsorption thickness under similar conditions compared to low molecular weight of PEI. These changes of silica abrasive such as electrostatic forces and steric interaction vary with molecular weight of PEI reduced the dishing of Cu pattern film from 50 to 20 nm.

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1. Introduction

Chemical mechanical planarization (CMP) for interconnects in ultra large scale integration (ULSI) device has proven as a significant technique for achieving the uniformity of the wafer surface [1]. However, slurry including abrasives induces defects like dishing, erosion and scratches during the Cu CMP process due to the very soft nature of metallic Cu. Controlling the amount of dishing in the damascene process is crucial since it could decrease the conductivity [2,3]. Generally, silica abrasive has been used in Cu CMP, but the direct contact of hard abrasive particles on the Cu inevitably induces defects and dishing in CMP [4,5]. Various efforts have been devoted to overcome the limitations arising due to defects and dishing which includes the integration of Cu electro-polishing with a wetetching technology [6,7], abrasive-free polishing [8–10], and application of core-shell structured abrasive [11–13]. Armini

et al. prepared PMMA core-silica shell abrasives by using coupling agents and electrostatic attraction in order to form the core-shell. In the case of a soft pad in combination with modified abrasives, it shows a remarkable improvement in the defectivity without ant loss in MRR [11]. However, there are few studies in the literature which focus on the effect of the electrostatic forces and steric interaction of polymeric modified silica abrasive on Cu CMP performances. In this study, the effect of polymeric modified silica abrasive on Cu CMP was identified with changes of electrostatic forces and steric interaction, which were controlled by the physico-chemical behavior between polymer and silica abrasive [14]. Many researchers have studied to modify silica surface with polymer such as Poly(ethylene oxide) (PEO) [15,16], Poly(vinyl pyrrolidone) (PVP) [16,17], Polyacrylamide (PAAm) [18], and Poly(ethyleneimine) (PEI) [19–21]. Silica shows a negatively charged surface throughout the pH range 3.0–11 [22]. Cationic polymers have an advantage as modifier over nonionic polymers such as PEO and PVP. In the case of PAAm, very high adsorption amounts of PAAm on silica were observed in literature [18]. Toothick polymer layer on silica causes a decrease of removal rate of Cu. Thus, it is not suitable for CMP application. PEI is a cationic polymer due to the presence of amine groups and is used to change surface potential of negatively charged

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surface of silica abrasive [11,19–21]. This PEI adsorption layer prevents the silica abrasive from the direct contact on Cu [13]. Although PEI-modified silica shows a decreased the blanket removal rate of Cu film due to a decrease of the hardness of silica abrasive by PEI adsorption layer on silica abrasive, it shows the improved polishing performances of pattern wafer such as dishing. The steric interaction of PEI adsorption layer on silica abrasive induces to decrease the degree of dishing due to the low friction force by a decrease of the hardness of silica abrasive. Therefore, the polishing performances of pattern wafer were improved with slurry containing PEI-modified silica abrasive. As a control the physico-chemical behavior between PEI and silica abrasive vary with the molecular weight of PEI, the polishing performances of Cu CMP were identified. Also, PEI-modified silica abrasive was effective for preventing the formation of microscratches during Cu CMP.

2. Experimental

PEI (Sigma-Aldrich Inc.) with two different molecular weights of 2,000 and 25,000, respectively, were added in silica slurry at weight fractions of 0.5% to study the physico-chemical behavior vary with the molecular weight of PEI, which is used for the formation of an adsorption layer on silica abrasive. Commercially available silica slurry (PL-3, FUSO Chemical Co., Tokyo, Japan), which shows particles size with diameter of 35 nm. And 200 mm wafer deposited Cu film was used on the present investigation.

Adsorption isotherms for PEI on silica of 35 nm were determined at 25 ± 1 °C via the solution-depletion method using a total organic carbon (TOC) analyzer (5000A, Shimadzu Corp., Kyoto, Japan). Samples were prepared in deionized water containing a silica mass fraction of 5% and equilibrated with rolling for 12 h. The final pH value of the slurry was 7.0. The slurries were centrifuged and the supernatant was further clarified using a 0.02 μm Anotop 25 syringe filter (Whatman, Tokyo, Japan) and then analyzed in triplicate for TOC. TOC values were converted to polymeric molecule mass using an experimentally determined calibration curve. Adsorption isotherms were derived from the difference between the adsorbed amount and the polymer concentration in the supernatant.

The electrokinetic behavior of the silica slurry was characterized using the electrokinetic sonic amplitude (ESA) technique (ESA-9800, Matec Applied Sciences, Hopkinton, MA). Separate acid (1.0 N HCl) and base (1.0 N KOH) titrations were performed, beginning at pH 8, and were subsequently combined to generate a complete titration curve. Based on the analysis of the preliminary measurements, the standard uncertainties were ±0.1 mPa m V⁻¹ for the ESA measurements and ±0.05 (pH units) for the pH and pH_{iep} values, respectively.

To analyze the physico-chemical behavior of the PEI on the silicon oxide film, force-separation measurements were obtained using a commercial multimode atomic force microscope (XE-150, Park System, Korea). The Si atomic force microscopy (AFM) tip (SI-CONGG, AppNano) was used to investigate the interaction forces using contact mode. The spring constant of the cantilever provided by the manufacturer was 0.12 N/m. Also, SiO₂ film was prepared as the substrate with a size of 20 mm × 20 mm and immersed SiO₂ substrate in PEI solution for 20 min. Then solution with the same pH was used to remove the side effect by non-adsorbed polymer molecules. The concentration of the PEI solution was 0.5 wt%, and the final pH of PEI and washing solutions prepared in this study was 7.0. The force displacement curves were converted from deflection signal-piezo scanner movement data and averaged using data analysis software (XEI, Park System). The experimental procedure used in this study was the same as reported in our previous studies [23].

Table 1
Experimental conditions.

Slurry	Silica slurry
Solid concentration of slurry	5.0 wt%
Pad	IC1000 SUVAIV
Table speed	80 rpm
Down force	20.68 kPa
Flow rate	100 ml/min

The CMP field evaluation was performed using three kinds of slurries with PEI. A Cu coupon wafer (6 cm × 6 cm) CMP tool (POLI-300, G&P, Korea) was used. The polishing pad was a grooved IC1000/SubaIV (Rodel). The Cu film thickness was measured using a four point probe (CMT-SR2000N, Chang Min Tech, Korea) to calculate removal rates. The polishing test conditions are shown in Table 1.

To identify the surface properties such as microscratches and defects of Cu film after CMP, the optical images were taken by light microscopy (BX51, Olympus, Tokyo, Japan).

3. Results and discussion

Fig. 1 shows the adsorption isotherm of PEI on silica abrasive as function of molecular weight at pH 7.0. The experimental data was modeled using the linearized Langmuir adsorption isotherm equation.

$$C_e/Q_m + 1/bQ_m = C_e/Q_e$$

Q_e is the adsorbed amount of PEI per silica surface area at equilibrium (mg/m²), C_e is PEI concentration in the bulk solution (mg/L), Q_m is the maximum adsorbed amount (mg/m²), and b is the free energy constant of adsorption (L/mg). The silica slurry has a negative charge above pH 3.5, which is the isoelectric point of silica, and PEI has a positive charge since pKa of PEI is 10.5. Consequently, PEI is adsorbed on the silica most likely governed by electrostatic force. The adsorption follows a Langmuir isotherm that is as the concentration of PEI increases the adsorbed amount of PEI increases until it reaches a plateau region. The adsorbed amount of PEI 2,000 to (<350 mg/L) was almost 100%, followed by a flattening and reached a plateau level of 0.195 mg/m². In PEI 25,000, the adsorbed amount increased sharply at a low residual concentration and reached a plateau level of 0.228 mg/m². These results show PEI 25,000 has a higher affinity isotherm compared to PEI 2,000. We hypothesize that there are two factors contributing to a higher

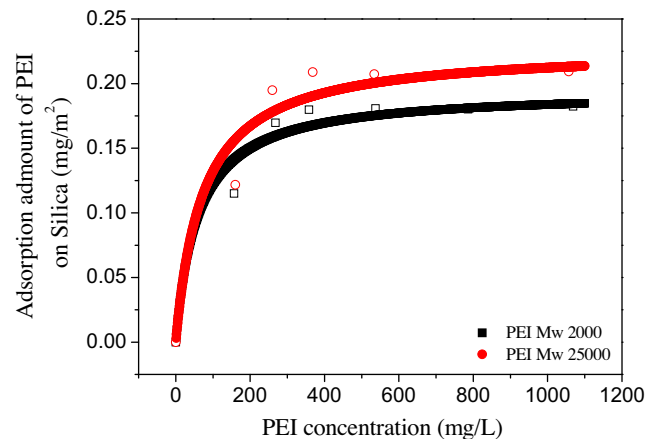


Fig. 1. Room temperature adsorption isotherms of PEI on silica abrasive at pH 7. Data was fitted with the Langmuir adsorption isotherm equation.

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