



Interpolymer complexes of poly(acrylic acid) and poly(ethylene glycol) for low dishing in STI CMP



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ABSTRACT

Although poly(acrylic acid) (PAA) has been used as a passivation agent for high polish rate selectivity between SiO_2 and Si_3N_4 in STI CMP, it causes severe dishing during the over-polishing step. Here, we fabricated interpolymer complexes of PAA and poly(ethylene glycol) (PEG) as passivation agent for low dishing as well as high selectivity. PAA and PEG form a cross-linked network structure through H-bonding, which is called an “interpolymer complex”. During the over-polishing step, the cross-linked network structure of the PAA-PEG interpolymer complex prevents abrasives from polishing SiO_2 in the trenches, resulting in a significant decrease in dishing. These results provide researchers with a new approach toward passivation agents to provide low dishing in STI CMP.

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1. Introduction

Shallow trench isolation (STI) is a crucial technology for enhancing the device packing density in ultra-large-scale integration (ULSI) fabrication [1–3]. Traditionally, in order to form STI structure, shallow trenches are made between active devices, and gap-filling materials such as SiO_2 are deposited over the trenches. After these processes, the step height of gap-filling materials is inevitably formed due to the different pattern density, which needs to be removed. Chemical mechanical planarization (CMP) process removes the step height of the gap-filling materials [4,5], and it is stopped on the Si_3N_4 film [6,7]. Contrary to these former STI CMP processes, current processes require an over-polishing step to completely remove SiO_2 on Si_3N_4 film because the number of maximum permissible defects has been decreased with recent developments in 40 nm node devices and beyond. Insufficient over-polishing leaves residual SiO_2 on the Si_3N_4 film, which causes transistor failure due to the remaining Si_3N_4 after the Si_3N_4 strip [8]. On the other hand, excessive over-polishing produces dishing because the removal rate of SiO_2 in the trenches is much higher than that of Si_3N_4 [8]. As the design rule decreases, the

requirements on CMP performance have become more stringent. Dishing, which has a significant influence on device performance, must be suppressed to improve device yield.

Poly(acrylic acid) (PAA), a water-soluble anionic polymer, has been widely used as a passivation agent for high polish rate selectivity between SiO_2 and Si_3N_4 [6,9–11]. It is preferentially adsorbed on the Si_3N_4 film through the attractive electrostatic force [12], resulting in the high selectivity between SiO_2 and Si_3N_4 . However, a significant difference in the removal rate between SiO_2 and Si_3N_4 causes a severe dishing during the over-polishing step.

Herein, we propose the PAA-poly(ethylene glycol) (PEG) interpolymer complex as a passivation agent for low dishing with high selectivity between SiO_2 and Si_3N_4 . PAA in aqueous solutions is sensitive to the changes in its physicochemical conditions including pH, ionic strength, and concentration. With mixtures of complementary polymers such as PEG [13–15], poly(acrylamides) [16], and poly(vinyl ethers) [17,18], it enables to the formation of the cross-linked network structures through the H-bonding, which is called “interpolymer complexes”. At pH values higher than 5.0, the interpolymer complex is dissociated due to the increase in the negatively charged carboxyl groups (noncomplexable sites) in the PAA [14,19]. On the other hand, at pH values lower than 3–3.5, the fraction of negatively charged carboxyl groups that significantly influence the solubility of the complexes decreases considerably, leading to the formation of precipitates. In this study, we have prepared the

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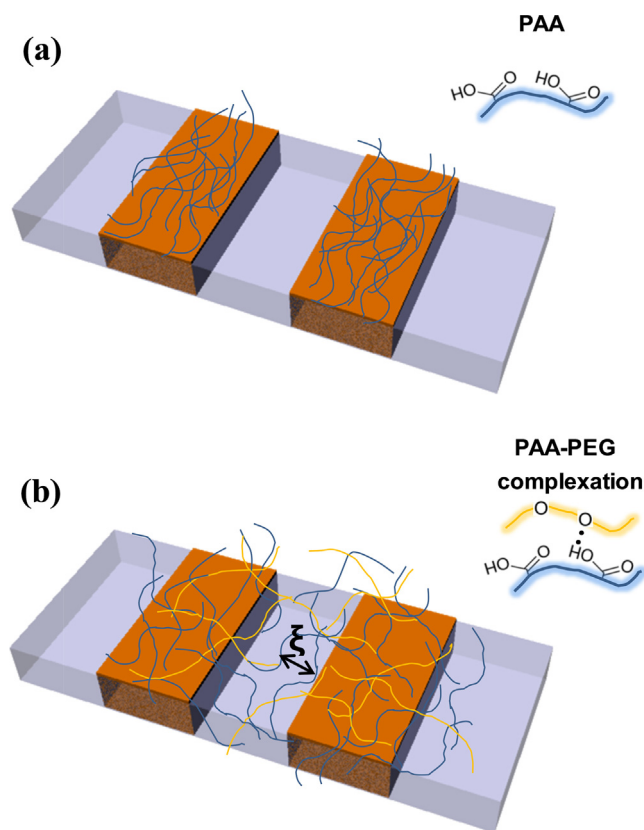


Fig. 1. Schematic illustrations of (a) PAA and (b) PAA-PEG interpolymer complex as passivation agents in STI CMP.

PAA-PEG interpolymer complexes at pH 5.0 considering their solubility and adsorption properties on the Si_3N_4 film.

Fig. 1 describes the schematic passivation mechanism to enable low dishing in STI CMP. PAA preferentially adsorbs on Si_3N_4 film, leading to the high selectivity between SiO_2 and Si_3N_4 . However, the SiO_2 in the trenches is removed during over-polishing, which causes a significant dishing. Contrary to PAA, we expect that the PAA-PEG interpolymer complex can prevent abrasives from polishing SiO_2 in the trenches. When the Si_3N_4 film is exposed during polishing, the noncomplexable negatively charged carboxyl sites in the PAA-PEG interpolymer complex adsorb on the highly positively charged Si_3N_4 film at pH 5.0 through the attractive electrostatic force [12,20]. During polishing, it is difficult for the abrasives to penetrate the cross-linked network of the interpolymer complexes, which leads to the low removal rate of SiO_2 in the trenches. As a result, dishing is significantly decreased.

2. Experimental

2.1. Suspension preparations

PAA ($M_w \approx 5000$, Polyscience, Inc.) and PEG ($M_n \approx 4600$, Sigma-Aldrich) were used as received without further purification. PAA-PEG interpolymer complex solutions were prepared at 0.8 wt% PAA as a function of PEG concentration (0, 0.1, 0.2, and 0.3 wt%). The pH was adjusted to 5.0 by addition of NH_4OH solution. The solutions were aged for 12 h at room temperature using a mixer (Ball mill, Nanointech, Korea). Solid-state ceria slurry (KCS3100, Korea) was obtained from K.C.Tech Co., Ltd. Transmission electron microscopy (TEM) image of solid-state ceria is shown in Fig. S1 in the Supplementary data.

Table 1
CMP conditions.

Experimental conditions	
Slurry	KCS3100
Solid concentration of slurry	1.0 wt%
Pad	IC 1000/Suba IV
Spindle/Table speed	70/70 rpm
Down force	2 psi
Polishing time	60 s
Flow rate	Slurry 50 mL/min; Additive 50 mL/min

2.2. Characterization methods

To identify the characteristics of PAA-PEG interpolymer complexes, Fourier-transform infrared spectra were recorded in the range $4000\text{--}500\text{ cm}^{-1}$ with a FT-IR Spectrometer (Nicolet 5700, ThermoElectron, US) using KBr pellet method. Four different interpolymer complex solutions were dropped on KBr powder, and then dried in an oven during 6 h at 80°C . Samples were grounded into a fine powder using agate mortar and pestle, and pellets were made from them.

The viscoelastic properties of PAA-PEG interpolymer complexes were measured by rheometer (MCR 501, Anton Paar, Germany) at 25°C using the cylindrical double-gap configuration (DG-26.7). An oscillation strain sweep was carried out in a strain range from 0.1% to 1000% (logarithmically) at 1 rad/s angular frequency (ω). The storage modulus G' and the loss modulus G'' were examined in the range of ω from 0.1 to 100 rad/s at the linear visco-elastic region (constant strain of $\gamma = 10\%$).

TEM image of solid-state ceria was observed using a field emission TEM (JEM-2100F, JEOL, Japan). Particle size distribution of solid-state ceria slurry without and with PAA-PEG interpolymer complex solutions was determined by dynamic light scattering (DLS) at a scattering angle of 173° (Zetasizer Nano-ZS, Malvern, UK) at 25°C .

2.3. Chemical mechanical planarization (CMP)

The blanket SiO_2 and Si_3N_4 films were prepared by deposition on the 200 mm Si wafers using plasma enhanced tetraethyl orthosilicate (PETEOS) and low pressure chemical vapor deposition (LPCVD), respectively. To prepare STI patterned wafer, 800 Å Si_3N_4 films were deposited on the 200 mm Si wafers using LPCVD, etched about 1000 Å to fabricate the trenches. And SiO_2 were deposited 2000 Å using PETEOS method. To remove the step height of SiO_2 , the patterned wafers were polished using commercial slurry (KCS1200MS, K.C.Tech Co., Ltd., Korea) for step height reduction. These wafers were cut into $6\text{ cm} \times 6\text{ cm}$ pieces for coupon-polishing.

The wafer pieces were polished for 1 min in CMP tool (POLI-300, G&P Tech. Inc., Korea) with an industry standard CMP pad (IC 1000/Suba IV, Rohm and Haas Electronic Materials, USA). The CMP evaluations were performed using four different PAA-PEG interpolymer complex solutions with the commercial solid-state ceria slurry. Down pressure and spindle/table speed was 2 psi and 70/70 rpm, respectively. Both flow rates of slurry and chemical solutions were 50 mL/min, and the polishing time was 60 s. Each CMP evaluation was repeated 2 times. The polishing test conditions are summarized in Table 1. After CMP, the wafers were cleaned in an alkaline environment and then dried. The removal rates of the blanket SiO_2 and Si_3N_4 films were determined by measuring before and after film thickness using an ellipsometer (MM-16, Horiba Jobin Yvon, France). The dishing of the patterned wafers were measured by a multimode atomic force microscope (XE-150, Parksystem, Korea) with an Al coated PPP-NCHR cantilever in non-contact (NC-AFM) mode. Surface properties such as microscratches and defects

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