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Charge Density and pH Effects on Polycation Adsorption on Poly-Si, SiO_2, and Si_3N_4 Films and Impact on Removal During Chemical Mechanical Polishing

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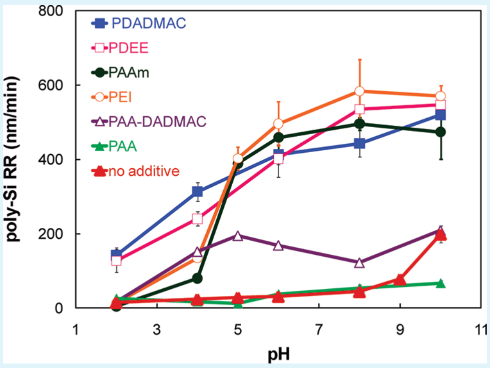
ABSTRACT: The pH-dependent interactions of five aqueous abrasive-free polycationic solutions, all at a concentration of 250 ppm, with poly-Si, SiO_2, and Si_3N_4 films and IC1000 polishing pads used in chemical mechanical polishing have been investigated and compared with the interaction of poly(diallyldimethyl ammonium chloride) (PDADMAC) that was investigated recently. Three of the polycationic solutions, poly(dimethylamine-co-epichlorohydrin-co-ethylenediamine), poly(allylamine), and poly(ethylene imine) (PEI) enhance poly-Si removal rates (RRs) to the range of about 500 to 600 nm/min at pH 10. In contrast, poly(acrylamide) (PAA) suppressed poly-Si RRs to about 50 nm/min, whereas with a copolymer of PAA and PDADMAC, the RRs were lower than those obtained with PDADMAC but higher than those obtained with PAA. For all the polycationic solutions, the RRs of both SiO_2, and Si_3N_4 films were ~0 nm/min. These solutions offer a low-defect option for the processing of emerging FinFET devices. The variation in the RR magnitude and dependence on pH among the different polycations is related to the relative charge density of the polycations as well as the films being polished, consistent with ζ potential data. Based on the ζ potential data and earlier published reports, it is suggested that the strong polycation-mediated bridging interactions between the polarized and weakened Si—Si bonds of the poly-Si surface and the polyurethane IC 1000 pad are responsible for the high poly-Si RRs.



KEYWORDS: abrasive-free polycationic solutions, bridging interaction, charge density, pH, CMP, poly-Si, SiO_2, and Si_3N_4

1. INTRODUCTION

Polysilicon (poly-Si) is used as a part of the gate electrode in the 3D nonplanar Fin field-effect-transistors (FinFET) structures that were proposed to replace classical planar single gate metal-oxide-semiconductor (MOSFET) for reducing short channel effects and facilitate further scaling.[1−3] It is also used as a floating gate in NAND flash cells,[4] as a sacrificial layer in the metal gate replacement technique[5] during the fabrication of high-K metal gate MOSFET devices, and as a structural element for movable parts in microelectromechanical systems (MEMS).[6−8]

During the fabrication of FinFET, NAND flash memory, and MEMS devices, one of the major challenges is to achieve local and global planarization by removing the large step heights of poly-Si layers. As it is well-known, the only viable technique for this purpose is chemical mechanical planarization (CMP). During the CMP process, the overburden poly-Si has to be selectively planarized over the underlying oxide/nitride patterns.[9−12] This step requires a slurry which produces high poly-Si removal rates (RRs) and very low oxide and nitride RRs (~ 1 nm/min or lower). In contrast, during the fabrication of a high-k/metal or a poly-Si/SiO_2 gate, a poly-Si structure is initially placed as a dummy gate upon which nitride[9−12] or oxide[13] is deposited, and the excess material is removed by a CMP process. This poly-Si-open CMP process requires high polish rates of nitride or oxide material or both, while stopping on the poly-Si surface. This can be achieved using an oxide and nitride polishing slurry that also provides very low poly-Si RRs (<5 nm/min). In view of the importance of these processes, considerable work has been done to develop slurries that can provide these two different options.[14−24]

For example, Dandu et al.[14−16] reported that various amine- and amino acid-based slurries, with and without ceria/silica abrasives, can selectively polish poly-Si over oxide and nitride films. We also showed that high poly-Si RR selectivity over oxide and nitride films, again useful for FinFET and MEMS fabrication, can be obtained using an abrasive-free aqueous solution of poly(diallyldimethylammonium chloride) or PDADAMC.[17,18] At a very low PDADMAC concentration of 250 ppm, the poly-Si RR is ~500 nm/min at pH 10, and the oxide and nitride RRs are ~0 nm/min. Interestingly, the addition of ceria abrasives had no effect on these RRs, while the poly-Si RRs are slightly higher with silica abrasives. In contrast, several researchers reported that silica- and ceria-based slurries can suppress poly-Si RRs with varying oxide and nitride RRs.[19−21]

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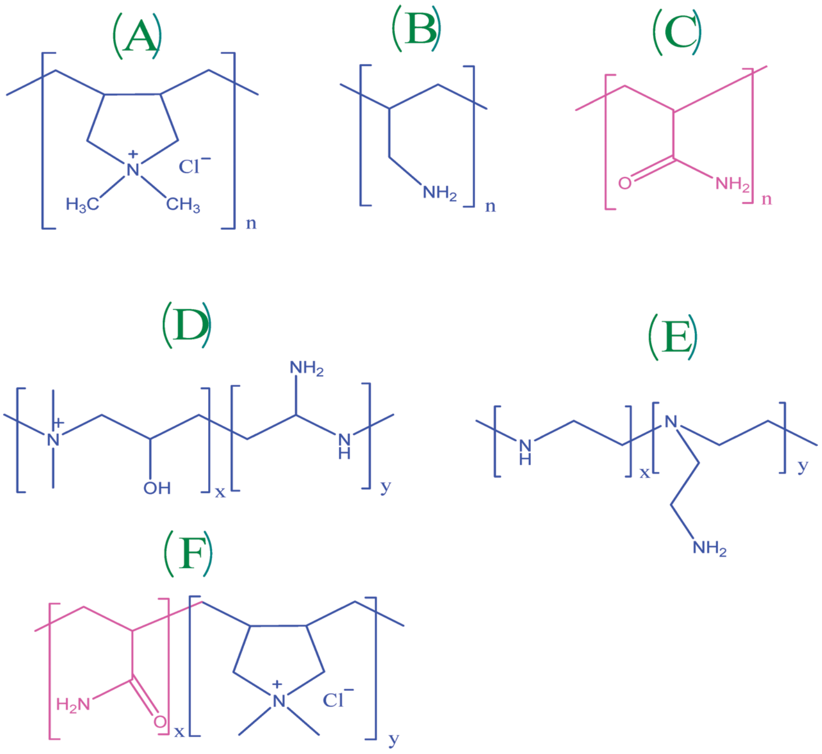

Figure 1. Schematic structures of the different polycations used here: (A) PDADMAC (Average molecular weight (M_w) ≈ 200 000−350 000), (B) PAAm (M_w ≈ 15 000), (C) PAA (M_w ≈ 1500), (D) PDEE (M_w = 75 000), (E) PEI (M_w ≈ 800), and (F) PAA-DADMAC (M_w ≈ 250 000).

Using abrasive-free aqueous solutions during CMP can eliminate contaminants, mobile ions, and various defects, scratches and structural damage to the surface that can be caused by abrasives, and at the same time potentially lower the costs. Indeed, Xiaolin[25] experimentally showed that the poly-Si feature recess can be controlled when only pad asperities, not the abrasives, are used for the polishing process. Hence, we investigated several aqueous polycationic solutions besides PDADMAC and discovered that abrasive-free aqueous solutions of several cationic polymers, namely, poly(dimethylamine-*co*-epichlorohydrin-*co*-ethylenediamine) or PDEE, poly(allylamine) or PAAm, poly(ethylene imine) or PEI, poly(acrylamide) or PAA, and poly(acrylamide-co-diallydimethyl ammonium chloride) or PAA-DADMAC, in addition to PDADMAC (all shown in Figure 1), have very desirable polishing characteristics. Among these, PDEE, PAAm, and PEI solutions enhanced the poly-Si RRs to the range of ∼500−600 nm/min at pH 10, similar to PDADMAC. In contrast, PAA solutions suppressed them to ∼50 nm/min, whereas PAA-DADMAC solutions produced RRs that are intermediate between those obtained using PDADMAC and PAA. It is worth noting that even though several studies[22−24] used PEI and PAA as additives in either ceria- or silica- based slurries for selective polishing of poly-Si over oxide, none of them reported that PEI alone enhances the poly-Si RRs or that PAA alone suppresses them. In all the experiments described here, only abrasive-free aqueous solutions were used during polishing.

It is known that these polycationic molecules can generate strong bridging interactions between the dielectric films and the polymeric pads, consisting essentially of polyurethane, used during CMP.[17,18] These interactions are discussed in the following at some length based on ζ potential and contact angle measurements. We also discuss possible mechanisms for the removal of poly-Si at a high rate and of oxide and nitride films at a negligible rate when polishing with these polymer solutions.

2. EXPERIMENTAL METHODS

2.1. Materials. All the polymers, silicon nitride particles (d_{mean} ≈ 50 nm) and pH adjusting agents (HNO_3 and KOH) used here were obtained from Sigma-Aldrich. Colloidal silica particles (d_{mean} ≈ 50 nm) were supplied by Nyacol Technology. The polishing pads (IC1000) and the diamond-grit conditioner were supplied by Dow Electronic Materials and 3M, respectively. Blanket poly-Si wafers (2000 nm thick, low pressure chemical vapor deposited or LPCVD, at ∼610 °C) were obtained from DK Nanotechnology. Thermal oxide (2000 nm thick, grown at ∼900 °C) and silicon nitride (500 nm thick, LPCVD at ∼790 °C) films grown on silicon substrates were obtained from Montco-Silicon Technologies, Inc. While the poly-Si and silicon nitride films were deposited on an intervening 100 nm thick silicon dioxide layer grown on 8 in. diameter silicon wafers, the thermal oxide was directly grown on the silicon substrate. Each of these 8″ wafers were cut into several 2 in. diameter pieces, which were then used for polishing.

2.2. Polishing Experiments. The 2 in. diameter wafers were polished for one minute on a CETR polisher at 4 psi down pressure, 90/90 rpm carrier/platen speed, and a slurry flow rate of 120 mL/min. The IC1000 pads (k-groove) used in the polishing experiments were conditioned for one minute using a 4″ dia diamond-grit conditioner after every polishing experiment. A Filmetrics interferometer was used to measure the thickness of the different films (oxide, nitride and poly-Si) before and after polishing. The RR of each of these films was determined from the difference between pre- and postpolished film thickness values measured for two different wafers, each at 16 points located across a diameter of the wafer, and then averaged. The standard deviation in the RRs was based on the data for these 32 points. The pH of all the

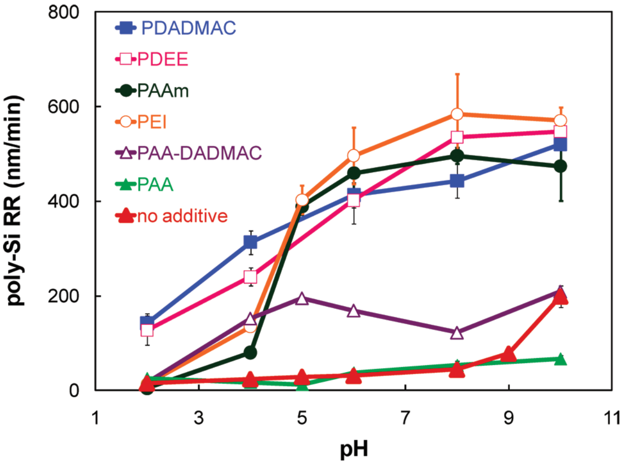

Figure 2. RRs of poly-Si films as a function of pH on an IC1000 pad using pH-adjusted DI water and aqueous solutions containing 250 ppm of the polyelectrolytes.

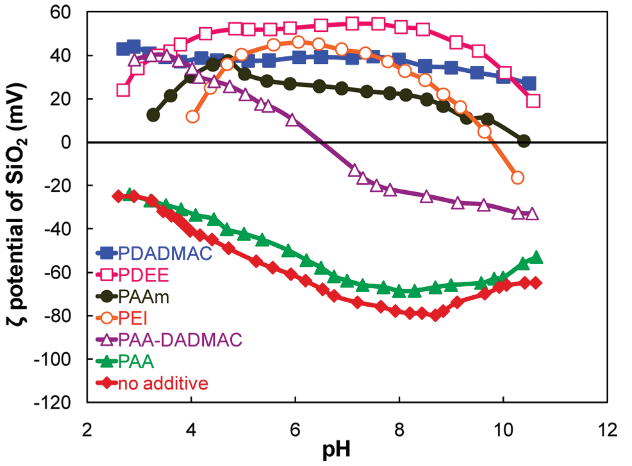

Figure 3. ζ potentials of 1% silica ($d_{\mathrm{mean}} \approx 50$) dispersion in the absence and presence of 250 ppm of each of the polyelectrolytes.

polycation solutions was adjusted by adding small amounts of KOH or HNO_3.

2.3. Contact Angle Measurements. A goniometer, assembled on a vibration-free optical table coupled with CAM software (KSV instruments Ltd., Finland) was used to measure the contact angle of a water drop on pre- and postpolished films. Before the measurement, the polished wafer was dried using an air jet. The reported contact angle is the average of 3−4 measurements at three different locations on the wafer (center, middle and edge).

2.4. ζ Potential Measurements. A Matec Applied science model 9800 Electro acoustic analyzer was used to measure the ζ potentials of 1 wt % silica and 1 wt % silicon nitride particles in the absence and presence of each of the polymers as a function of pH. Nitric acid was used to lower the pH while potassium hydroxide was used to increase the pH of the dispersion. The ζ potentials of a small piece of an IC1000 pad and of a poly-Si film, in the absence and presence of all these polymers, were determined using a ZetaSpin 1.2 apparatus (Zetametrix, Inc., USA). In this technique, the ζ potential is calculated from the streaming potential measured in the vicinity of a rotating disk with aqueous KCl (0.001 M) as the background electrolyte. The apparatus and method were described by Sides et al.[26] Because this instrument requires a 1″ diameter sample with a flat smooth surface, a sample from the IC1000 pad was obtained from the center of the pad, where there are no grooves.

3. RESULTS AND DISCUSSION

3.1. Polishing Data. Figure 2 shows the RRs of poly-Si films obtained using the six different polycationic-based aqueous solutions, all at 250 ppm concentration, in the pH range 2−10. This concentration was chosen for all the experiments so that the RRs of poly-Si can be compared with those obtained earlier at this concentration with PDADMAC.[17,18]

Using only pH-adjusted deionized water, the RRs of poly-Si were low for pH ∼≤6 and increased beyond this pH reaching about 200 nm/min at pH 10 due to the increase in the concentration of OH^- ions which attack Si−Si bonds and break them.[27−29] However, as reported earlier, 250 ppm PDADMAC aqueous solutions enhance the poly-Si RRs significantly throughout the pH range of 2−10.[17,18] Here we find that PDEE aqueous solutions also enhance the poly-Si RRs and, more or less, to a similar extent in the entire pH range. Furthermore, both PAAm and PEI solutions also enhance the poly-Si RRs significantly, but only for pH ≥5. At lower pH values, the RRs dropped and remained lower than those obtained with PDADMAC and PDEE.

In contrast, when PAA solutions were used, the poly-Si RRs did not change much in the pH range 2−8 when compared to those obtained using only pH-adjusted DI water, and, even more interestingly, the poly-Si RR was suppressed to ∼50 nm/min at pH 10, lower than the ∼200 nm/min obtained without PAA. Furthermore, using the copolymer of PAA and PDADMAC, the poly-Si RRs were lower than those obtained with PDADMAC but higher than those obtained with PAA for pH > 2.

Unlike the poly-Si RRs, both the oxide and nitride RRs were ∼0 nm/min when polished using pH-adjusted DI water in the pH range 2−10 as reported earlier,[17,18] and they also did not change much throughout the pH range when polished using 250 ppm of aqueous solutions of any these polymers. These data are not shown.

Thus, it is worth noting that the aqueous abrasive-free solutions of PDADMAC, PDEE, PAAm, and PEI at only 250 ppm concentration can provide a selectivity of poly-Si RR over both oxide and nitride RRs that is useful for the fabrication of FinFET, NAND flash memory and MEMS devices. Before discussing these various RRs and their dependence on pH, it is necessary to understand the adsorption of these polycations on the films being polished (poly-Si, oxide and nitride) as well as the polishing pad. We start with a discussion of the measured ζ potential variations with pH caused by the adsorption of the different polycations on these surfaces.

3.2. Adsorption of the Polymers on Silicon Dioxide Surfaces and Its Effect on ζ Potentials. Figure 3 shows the ζ potentials of aqueous dispersions of 1% silica ($d_{\mathrm{mean}} \approx 50$ nm) in the absence and presence of 250 ppm of each of the polymers. In the absence of any additive, the silica surface is negatively charged throughout the pH range 2.5−10.[17] On adding 250 ppm PDADMAC, the charge on the particles was reversed presumably due to the electrostatic adsorption of the $^+N(CH_3)_3$ groups of PDADMAC, as shown by Li et al.[30] ζ potential remained positive in the entire pH range, with very little dependence on pH, consistent with the reported pH-independence of PDADMAC charge density.[31−34] Bauer et al.[31−33] also reported that the silica surface charge can be reversed by PDADMAC at pH 2, 5.8, and 10.5. They postulated that PDADMAC adsorption is governed by electrostatic as well as

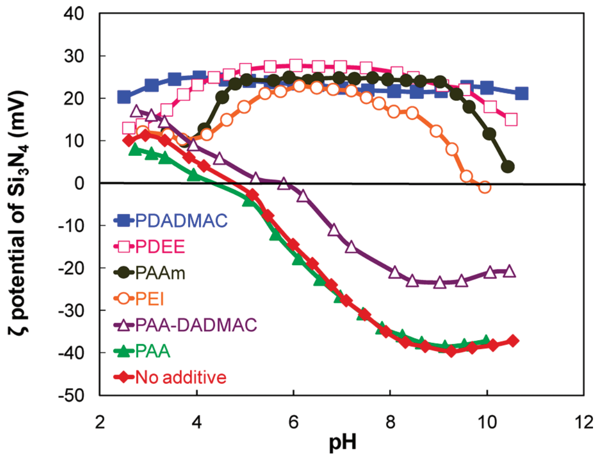

Figure 4. ζ potentials of 1% silicon nitride ($d_{\text{mean}} \approx 50$) dispersion in the absence and presence of 250 ppm of each of the polyelectrolytes.

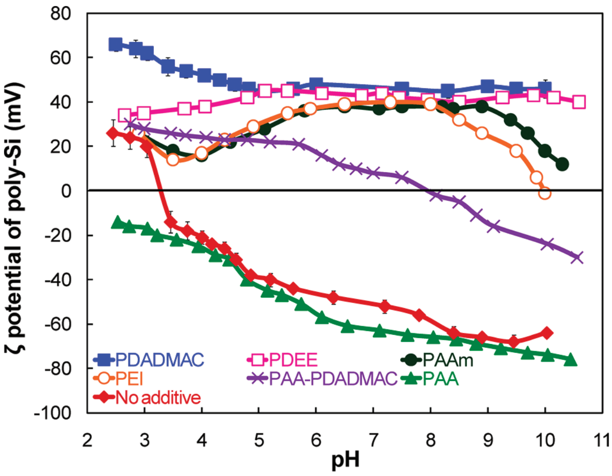

Figure 5. ζ potentials of poly-Si films in the absence and presence of 250 ppm of each of the polyelectrolytes.

chemical interactions between the surface and the polymer segments. Shin et al.[34] also observed a similar influence of this polymer on the surface charges of alumina: the surface charge was reversed and ζ potentials were maintained at ~60 mV at 1 wt % PDADMAC loading, even though the adsorbed amount increased with pH.

In the presence of PDEE, PAAm, or PEI also, the charge of the silica surface was reversed, presumably due to the adsorption of the amine groups of the polymer segments through electrostatic attraction or hydrogen bonding, as suggested by several studies.[35−38] Indeed, ζ potentials reached even higher positive values with PDEE than those obtained with PDADMAC for 4< pH <10 (Figure 3). However, ζ potential values declined for lower and higher pH values, and this pH range is polymer specific. For example, in the case of PEI, the higher ζ potential values were for 5< pH < 7, and the maximum was observed at pH ~6. Meszaros et al.[37] also observed a similar maximum of the ζ potential's with pH when PEI was added to silica dispersions. They also showed that, as the pH is increased, the degree of protonation of the amine group decreases and the amount of PEI adsorbed on silica increases, both monotonically, resulting in a maximum in ζ potential at some intermediate pH value.[38] PDEE and PAAm also exhibit a similar behavior of the electrokinetic potential, perhaps for the same reasons.

PAA is different from the other polymers since it is essentially nonionic in the pH range 2−10 that is of interest here. Nevertheless, it does adsorb on silica particles[39,40] as well as on various mineral surfaces,[41] and it was found that the amount adsorbed decreases with increasing pH due to the hydrolysis of the silanol groups on silica abrasives. Also, it was reported that the adsorption energy is weak.[42,43] On adding PAA (250 ppm), the negative ζ potentials of the silica surfaces were lowered only slightly for pH >3, presumably because of a shift in the slip boundary layer by the polymer layer adsorbed through hydrogen bonding as suggested by several studies.[44−46] This is contrast to the other positively charged polymers, for which the ζ potential variation is mainly due to the compensation of the silica surface charge by the opposite charge on polymer segments.

On adding 250 ppm of a copolymer of PDADAMC and PAA, the IEP of silica was observed to be between pH 6 and 7. More interestingly, the ζ potential values of silica at low pH are similar to those with PDADMAC. Bauer et al.[31−33] suggested that, at lower pH values, the surface charge densities are the same for particles covered with both PDADMAC and PAA-DADMAC, presumably due to both having the same numbers of adsorbed polymer charges. At higher pH, unlike PDADMAC, PAA-DADAMC does not dissociate the silanol groups further on the silica surface. Hence, less polymer is adsorbed and the ζ potentials remain low.

3.3. Adsorption of the Polymers on Silicon Nitride Surfaces and Its Effect on ζ Potentials.

Figure 4 shows the ζ potentials of 1% silicon nitride ($d_{\text{mean}} \approx 50$ nm)-based aqueous dispersions in the absence and presence of 250 ppm of each of the polymers. In the absence of any additive, the IEP of silicon nitride is ~5. Interestingly, in the presence of all these polymers, the behavior of the ζ potentials of the silicon nitride dispersions as a function of pH is very similar to those of silica dispersions except for one noticeable difference. In the presence of PDADMAC or PDEE or PAA-DADMAC, charge uptake seems to occur even below the IEP where electrostatic repulsion would be expected between the positively charged silicon nitride surface and the cationic PDADMAC molecules, indicating the existence of a strong chemical interaction between them. Malghan et al.[47,48] observed a similar behavior in the ζ potentials of silicon nitride dispersions when quaternized poly(diamine epoxychlorohydrin), a cationic polymer similar to PDEE, was used,. They proposed that the primary adsorption mechanism below the IEP is hydrogen and/or chemical bonding between the cationic polymer and the nitride surface while above the IEP, it was attributed to the electrostatic adsorption. Finally, in the presence of PEI, Jung et al.[49] observed dependence of the ζ potential of silicon nitride on pH that is similar to that shown in Figure 4.

3.4. Adsorption of the Polymers on Poly-Si Films and Its Effect on ζ Potentials.

Much more important for our discussion is the adsorption on poly-Si surfaces. The ζ potentials of a poly-Si wafer in the absence and presence of 250 ppm of each of the polymers were measured using the ZetaSpin instrument and the results are shown in Figure 5. The IEP of poly-Si is ~3.3. The same positive ζ potential values of poly-Si in the presence of PDADMAC were reported earlier.[17] The dependence of the ζ potentials of poly-Si on pH with PDEE, PAAm, PEI, PAA, and PAA-DADMAC is similar to that of silica and silicon nitride surfaces, and similar explanations for the pH-dependence of the ζ potentials above are valid. Also, unlike in the case of silica and silicon nitride particles, hydrophobic−hydrophobic

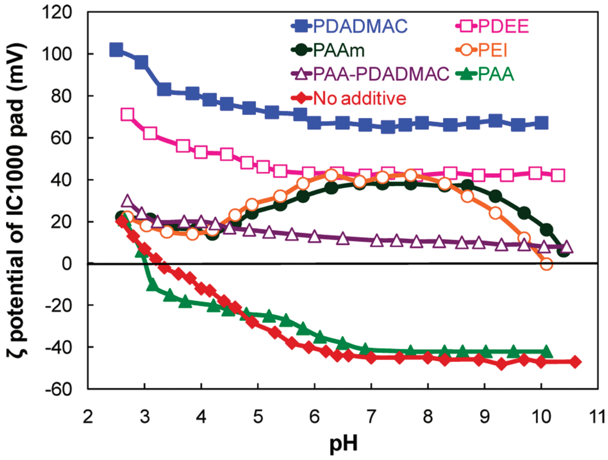

Figure 6. ζ potentials of an IC1000 pad in the absence and presence of 250 ppm of each of the polyelectrolytes.

interactions can also affect the adsorption of these polymers on poly-Si surfaces and modify ζ potentials, especially with PDADMAC.[17,50]

3.5. Adsorption of the Polymers on an IC1000 Pad and Its Effect on ζ Potentials. Figure 6 shows the ζ potentials of an IC1000 pad (for our discussions here essentially a polyurethane), also measured using the ZetaSpin instrument, in the absence and presence of 250 ppm of each of the six polymers. In the absence of any additive, similar ζ potential values of an IC1000 pad were reported earlier.[17,51,52] The effect of PDADMAC, PDEE, PAAm, PEI, PAA, and PAA-DADMAC on the ζ potentials of the pad is again very similar to that on oxide, nitride and poly-Si films. Most likely, this is due to interaction of these polymers with the pad surface is through electrostatic and/or hydrogen bonding with hydrolyzable groups (ester, amide, and polyurethanes)[18,53,54] on the pad surface being similar to that with the silanol and silanolate groups on the oxide, nitride and poly-Si surfaces. Hence, the pH-dependence of the ζ potentials of the pad in the presence of these polymers is also very similar to that of seen with these surfaces. Furthermore, hydrophobic−hydrophobic interactions also augment the electrostatic interaction and/or hydrogen bonding and increase the adsorption strength of these polymers on the IC1000 pad,[55] as in the case of poly-Si.

3.6. Contact Angle Data. Before polishing, contact angles on both the oxide and nitride films are ∼20°. After polishing with 250 ppm of any of the polymers solutions, the oxide and nitride films became very hydrophilic since the water drop quickly spread out. Same thing happened with the polished poly-Si films also, even though the contact angle of a water drop on a virgin poly-Si wafer, determined mostly by the Si−H terminal groups on a poly-Si surface,[56,57] is higher at ∼60°. These results confirm that all the polymers used here interact with the oxide, nitride, and poly-Si surfaces as suggested by ζ potential data.

4. POLISHING MECHANISMS

4.1. Proposed Mechanism for Poly-Si Removal in Presence of Aqueous Polymer Solutions and the Role of Polymer Charge Density. We discuss here a possible overall mechanism of poly-Si removal with the different polymer solutions and then in the next section, the RR variation with pH. Pietsch et al.[27−29] developed a model for removal of silicon that is applicable in the absence of any additive in the silica slurry during the polishing process. They suggested that OH^- in the slurry attack both Si−H and Si−Si bonds to form Si−OH structures, which polarize the adjacent Si−Si bonds. These polarized Si−Si bonds are attacked and broken by H_2O molecules. Using Fourier transform infrared spectroscopy, they showed the formation of subsurface oxygen bridges between Si−Si bonds aided by the dissolved oxygen in the ambient slurry. The interface between these suboxide structures and the underlying silicon is also weakened by H_2O molecules enabling their facile removal during polishing after which the process starts all over again.

This model was adapted by Dandu et al.[58] to explain the poly-Si RR enhancement upon the addition of α- amines or amino acids. They suggested that the adsorption of these additives on the poly-Si surfaces further polarizes and weakens the underlying Si−Si and accelerates the formation of suboxide, both leading to high material removal. Recently, we applied this model to explain the poly-Si RR enhancement obtained when PADMAC solutions were used.[17,18] Using zeta potential measurements, we proposed that PDADMAC binds to the poly-Si surface and to the IC1000 pad, resulting in a strong bridging interaction between the two surfaces that is mediated by the adsorbed PDADMAC molecules. Based on the measured poly-Si RRs, we hypothesized that the bridging interaction is stronger than the underlying weakened Si−Si bonds of the poly-Si surface. These weaker bonds are ruptured during polishing, resulting in accelerated material removal.

The ζ potential data and the earlier discussions suggest that the other five polymers under consideration also adsorb on the poly-Si film as well as the IC1000 pad. Thus, it is very likely that they also create a similar bridging interaction between the poly-Si and the IC1000 pad surfaces but only PDEE, PEI, and PAAm produced high poly-Si RRs, whereas PAA and PAA-DADMAC produced low poly-Si RRs. Presumably, the strength of the bridging interaction is polymer dependent.

There are several studies[59−63] that show that the pull-off force, a related measure, determines the strength of the bridging interaction and is influenced by the charge density of the polycation. Indeed, this has been measured and investigated theoretically in the case of mica surfaces.[63]

For example, using a copolymer of acrylamide (AA) and positively charged 3-(2-methylpropionamido)propyltrimethylammonium chloride (MAPTAC), Rojas et al.[59] studied the effect of the charge density of the polymer on its adhesion strength on mica surfaces. By changing the ratio of MAPTAC/AA segments of the copolymer, they were able to vary the charge density and observed that the pull-off forces between the mica surfaces decreased as the charge density of the copolymer decreased. For instance, the magnitude of the pull-off force needed to separate the polymer-coated mica surfaces dropped from ∼300 mN/m to only ∼5 mN/m when the polymer was changed from fully charged MAPTAC to a 30% charged 3:7 mixture of MAPTAC and AA. Also, Poptoshev and Claesson[60] showed that the pull-off forces with branched-PEI molecules are stronger than those with the two linear polymers, polyvinyl amine and poly(2-propionyloxy ethyltrimethylamonium chloride). The latter ones are very similar to PAAm and PDEE, respectively. Evidently, the charge density is a critical parameter.

Therefore, because the charge densities exhibited by each polymer can be categorized in the following sequence

$$\text{PDADMAC/PDEE/PAAm/PEI} > \text{PAA-DADMAC} > \text{PAA}$$

we suggest that the pull-off forces and, hence, the strength of the polycation-mediated bridging interaction between the pad and the films surfaces also follows the same sequence.

The high poly-Si RRs obtained using the high charge density cationic polymers, (PDADMAC, PDEE, PAAm, and PEI) shown in Figure 2 imply that the pull-off forces and, hence, the bridging interaction with these polymers is stronger than the strength of the underlying polarized Si−Si bonds. When the lower charge density copolymer of PDADMAC and PAA is used, the pull-off forces decrease and, hence, the removal rates are lower compared to those with PDADMAC. Finally, PAA induces the lowest pull-off forces among all the polymers since it has the lowest charge density, and hence, produces the lowest RR (Figure 2).

4.2. Variable Effect of pH on Poly-Si Removal with Different Polycations. Both PDADMAC and PDEE have a more or less constant positive charge density in the pH range 2−10 but the increasingly negative charge density of the poly-Si surface with increasing pH [Figure 5] can result in increased pull-off forces and, hence, increased RRs. Indeed, Holmberg et al.[61] and Osterberg[62] showed that polymer bridging is more favorable when the charge density on the opposite surface increases.

Same argument can explain the increasing RRs for pH $\gtrsim 5$ in the case of PEI and PAAm. But for pH <5, Meszaros et al.[37] found that the increased degree of protonation of the amine groups in PEI can increase the charge density but also lower the amount of PEI adsorbed on oxide surfaces because of the increased polymer segment−segment repulsion. In view of the similarity between PEI and PAAm, it is very likely that the same arguments apply for PAAm also. Hence, with these two polymers, the lowered amount of adsorption caused by segment−segment repulsion can decrease the number of bridging interactions between poly-Si and IC1000 pad. This in turn can result in a fall in the RRs, even though the pull-off forces are not affected much. In contrast, the quarternized ammonium ions in PDADMAC and PDEE do not protonate and only the charge density, but not the amount adsorbed, influences the RRs.

The RRs of poly-Si with PAA remain low and even lower than that with pH-adjusted DI water, suggesting that PAA adsorption blocks the effects of OH$^-$ that cause the increase in the RR with water.[58] Of course, the pull-off forces also are very weak. The dependence of the RRs of poly-Si with PAA-DADMAC on pH is complex and can be attributed to a combination of electrostatic interaction with the poly-Si surface changing from repulsive to attractive at lower pH values and the relatively weak bridging interactions.

4.3. Proposed Mechanism for Oxide and Nitride Removal in Presence of Aqueous Polymer Solutions. Previously, we suggested that even though PDADMAC forms a strong bridging interaction between the IC1000 pad and the oxide or nitride surfaces, the adhesive strength of the polymer on oxide, nitride and IC1000 pad is weaker than the cohesive strength of the oxide and nitride substrates.[17,18] Hence, during polishing, the polymer−substrate or the polymer−pad bond is broken easily, resulting in no material removal. Based on the RRs and ζ potential data, it appears that the same explanation also applies to polishing with other polymers here. It will be useful to verify this suggestion, perhaps using a suitably modified AFM probe tip and by studying the pull-off forces, but that is beyond the scope of this paper.

5. CONCLUSIONS

Similar to PDADMAC,[17,18] aqueous 250 ppm abrasive-free solutions of PDEE, PAAm, and PEI yielded high RRs of poly-Si films for pH values where the polycation charge density is high. However, for pH <4, the amino groups in PAAm and PEI are protonated lowering the adsorbed amount on the poly-Si surface due to segment−segment repulsion[37,38] and, hence, yield lower RRs. In contrast, PAA, essentially an uncharged polymer, produced the lowest RRs throughout the pH range, whereas a copolymer of PDADMAC and PAA, carrying intermediate charge density, produced intermediate RRs. Based on our ζ potential data and earlier published reports, it is suggested that the polycation-mediated bridging interactions[59−61] between the poly-Si surface and the polyurethane IC 1000 pad are responsible for the material removal during poly-Si polishing. The pull-off forces generated by these interactions during CMP appear to be stronger than the polarized and weakened Si−Si bonds in the films being polished and, hence, lead to high RRs. The strength of the bridging interaction is dependent on the charge density of the polycations[59] and pH.[38] Hence, in the pH region where the positive charge density of the polycation is high, the strength of the pull-off forces is high, resulting in higher RRs, and when it is low, the RRs are low. In case of silicon dioxide and silicon nitride films, the bridging interactions appear to be weaker than the underlying Si−O and Si−N bonds of oxide and nitride surfaces,[17] respectively, and none of these solutions cause removal. If the effectiveness of any of these solutions can be maintained while planarizing patterned structures, then it will be suitable for the fabrication of the recently announced 3D FinFET Si, MEMS and NAND devices.

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