Ceria-Based Slurries for Non-Prestonian Removal of Silicon Dioxide Films
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A slurry with a non-Prestonian dependence on the polishing pressure can help in minimizing dishing and erosion during shallow trench isolation chemical mechanical planarization. Here, we show that ceria-based slurries containing diallyldimethylammonium chloride (DADMAC) yield a non-Prestonian blanket film polish rate with a low threshold pressure (1–2 psi) when polishing plasma-enhanced chemical vapor deposition (PECVD) tetraethylorthosilicate (TEOS) deposited oxide as well as thermal oxide films. The polishing mechanism of this non-Prestonian slurry was investigated by a series of experiments involving zeta potential measurements, thermogravimetric analysis (TGA) and UV-vis spectroscopy and it was shown that more DADMAC molecules are adsorbed on silica particles (as oxide film representatives) than on ceria particles and the binding strength between DADMAC and silica is much higher than that with ceria particles.

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Shallow trench isolation (STI) is an ubiquitous complimentary metal-oxide semiconductor isolation process technology. Deposition of an isolation stack that contains 3 to 10 nm thick,12 thermally grown pad oxide on top of a silicon substrate followed by the deposition of either plasma-enhanced chemical vapor deposition (PECVD) or low-pressure chemical vapor deposition (LPCVD) nitride layer (10 to 30 nm)1 is the first step in the STI process. In the next step, active areas and isolation areas are determined by patterning the silicon nitride and silicon dioxide pad layers on the silicon substrate, followed by etching of trenches into the silicon substrate using the oxide/nitride stack as a mask. The trenches are then filled with oxide, employing high density plasma-enhanced chemical vapor deposition (PECVD) process using tetraethylorthosilicate (TEOS) as the source of silicon, because of its high gap-filling capacity. The deposited oxide not only fills the trenches but also generates an overfill, which needs to be removed. This is achieved through planarization of the oxide film topography by chemical mechanical planarization (CMP) using a slurry that produces a high oxide and very low nitride removal rates (RRs).

In this STI process, major concerns include dishing within the oxide features resulting from over-polish as well as the erosion of the underlying nitride film and, in some cases, the details of the corner rounding near active areas. Therefore, optimization of the CMP process is crucial in order to achieve complete removal of the oxide on top of the nitride film with good planarity and uniformity and to avoid erosion and dishing during the CMP process.3,4

One method that can be used to minimize dishing and erosion during STI CMP is to control the polishing performance by using a slurry that shows a non-Prestonian polishing behavior. Non-Prestonian behavior occurs when there is a non-linear relationship between applied polishing pressures and resulting polishing rates. Here we consider only the effect of pressure and not that of the rotational velocity on the blanket film polish rates.

Several models were discussed to describe the non-Prestonian behavior observed during copper as well as oxide CMP.3–9 Non-Prestonian RRs can occur in several ways, some of which are shown in Fig. 1. For example, the RR can increase linearly till a certain pressure is reached followed by a plateau (Fig. 1b) or the polishing rate is suppressed to a very low value below a threshold pressure above which the RR increases considerably, as shown in Fig. 1c to 1f. Kim et al.10 obtained the non-Prestonian polishing behavior shown in Fig. 1b by using a dispersion of rectangular shaped ceria particles to which polyacrylic acid (an anionic surfactant) was added. They reported that such slurries showed a linear increase of RRs up to 4 psi of applied down pressure after which the RRs reached a plateau and suggested that these kinds of slurries can be better for polishing “initial undulated areas”.

Our interest here is to obtain the non-Prestonian behavior illustrated in Fig. 1c–1f since these behaviors can, in principle, help to lower dishing and erosion. The non-Prestonian behaviors shown in Fig. 1c–1f ensure that the removal rate in the lower areas of various features will be low due to the low pressure exerted by the pad in these areas, especially for hard pads. It was already shown that a combination of line width, pattern density, pad rigidity and the applied down pressure determine not only the material removal rate but also the amount of dishing and erosion.5,6,8–11 Also, for CMP of Cu lines with an oxide spacer, Lin et al.3 modeled the effect of line width, pattern density, pad rigidity and applied down pressure on dishing and showed that the line width and the applied down pressure, but not pad rigidity or pattern density, have a more significant effect on dishing, and confirmed it experimentally. Indeed, it was also shown that the optimization of pressure settings during the polishing process can contribute to lower dishing.12

Here our interest is in identifying ceria-based slurries that can achieve non-Prestonian behavior for use in STI CMP. In addition to lowered dishing, such a slurry can also result in good planarization efficiency and lower nitride erosion.13 Ceria particles have already been used with various types of additives to obtain such non-Prestonian slurries for oxide CMP.14–17 For example, Nojo et al.14 reported that “self-stopping polishing” can be achieved by adding a surfactant (polyacrylic acid or ammonium polyacrylate) to a ceria slurry which also leads to a non-Prestonian, or “non-linear,” relation between the polishing pressure and the polishing rate. Kang et al.15,16 showed that varying the size (62–290 nm) of the ceria particles and the surfactant (polyacrylic acid) concentration (0.0–0.8 wt%) in the dispersions can alter the threshold pressure. They reported considerably high threshold pressures of ~4.5 and ~6 psi for ~170 nm and ~290 nm ceria particles respectively, below which oxide removal rate is low and above which the rate increases rapidly, but still linearly.17 However, it will be significantly beneficial to lower the threshold pressure, especially when the underlying structures contain fragile low-k and ultra-low-k films. Indeed, we show in the following that the addition of diallyldimethylammonium chloride (DADMAC) to ceria-based slurries leads to non-Prestonian blanket oxide film polish rates with a much lower threshold pressure of 1–2 psi. DADMAC is a quaternary ammonium compound which, because of electrostatic attraction, has a high tendency to form an adsorbed layer on an oxide film surface. This can result in non-Prestonian polishing behavior if a measurable threshold pressure exists for its removal during polishing. Our results show no RRs below ~1 and ~2 psi for 7.5 mM and 15 mM concentrations of DADMAC, respectively, in ceria dispersions. The
Figure 1. Representation of Prestonian and various non-Prestonian RRs: (a) Linear Prestonian rate passing through the origin; (b) to (f) are all non-Prestonian where (b) shows linear rate till a certain pressure is reached followed by a plateau and (c) to (f) show low or very low removal rate below a threshold pressure followed by a linear increase. The increase can also be non-linear.

RR increases linearly with increasing pressure above these thresholds. We plan to test this slurry with patterned structures and report these all important results later.

The polishing mechanism of this non-Prestonian slurry was investigated by a series of experiments involving zeta potential measurements, thermogravimetric analysis (TGA) and ultraviolet-visible (UV-vis) spectroscopy. The results of these measurements along with the polish rate data are described in the following.

Experimental

Chemical mechanical polishing (CMP).— Blanket silicon oxide films deposited on 8" diameter silicon wafers by plasma enhanced chemical vapor deposition (PECVD) using tetraethylorthosilicate (TEOS) as the silicon source as well as thermally grown (∼ 1050 °C) oxide films on 8" diameter silicon wafers were polished for 1 min on a POLI-500 polisher (G & P Technology, South Korea). Down pressures in the range of 1 to 4 psi, 87/93 rpm carrier/plate speed, and a slurry flow rate of 200 ml/min were used as the experimental conditions during polishing. The slurries were prepared using ceria particles (dmean ∼ 140 nm, Ferro Corp, USA) with and without DADMAC (Sigma-Aldrich). These particles were also used and described in our earlier investigations.18,19 The oxide RRs were determined by measuring the thickness of the films before and after polishing using a Filmetrics F-20 interferometer. The RRs were calculated from the average of the change in the thickness measured at 20 points across a diameter of the wafer, and the standard deviation reported was based on the data from total of 40 locations obtained from two different polished wafers. The polishing pad (IC1000, K-groove) was conditioned in-situ using a 4" diamond grid pad conditioner (S60, obtained from 3M Inc.).

Zeta potential.— The zeta potentials of 1 wt% ceria (dmean ∼ 140 nm) and 1 wt% silica (dmean ∼ 85 nm, used to mimic SiO2 films) dispersions with and without 25 mM of DADMAC were measured using a Matec Applied Science model 9800 Electro Acoustic analyzer. Silica and ceria dispersions with 25 mM DADMAC were prepared at pH 4. We use the higher DADMAC concentration - higher than that used in the polishing experiments - in these and other measurements below since even at a particle loading of only 1 wt%, the silica particles in the dispersion collectively have a relatively large surface area and consequently, more functional groups, than the oxide film surface on an 8" wafer.

All these dispersions (with and without DADMAC) were stirred for 10 min on a magnetic stirrer plate. The well-mixed slurries containing 25 mM DADMAC were centrifuged at 3000 rpm for 3 hours and the supernatants were decanted from sediments. The sediments were redispersed in deionized water adjusted to pH 4. This decanting and centrifugal washing process was repeated 5 times and the zeta potential was remeasured each time. Each zeta potential measurement was repeated 5 times and the averaged zeta potential of the first, third, fifth redispersions are reported here.

Thermogravimetric analysis (TGA).— Thermogravimetric analysis was done using a Perkin-Elmer Thermogravimetric analyzer, Pyris 1 to measure the amount of the additive (DADMAC) bound to the silica (representing SiO2 films) and ceria particles. The centrifugal process described above was used to collect the sediments from about 100 mL each of 1 wt% silica and 1 wt% ceria dispersions prepared with and without 10, 50 and 100 mM DADMAC. The collected sediments were dried in an oven at 70 °C for 48 hours. The dried samples were pulverized and then used for TGA measurements in an argon atmosphere. The temperature of the sample (∼50 mg) was initially raised to 100 °C and maintained there for 30 min to remove any residual moisture and the temperature was then increased to 400 °C at a rate of 15 °C/min while the sample weight was recorded. Decomposition temperature of pure DADMAC is between 175 and 247 °C.20 The reported weight loss data were normalized by subtracting the weight loss of the bare silica and ceria particles.

UV – visible spectroscopy.— Dispersions of 1 wt% ceria (dmean ∼ 140 nm) and 1 wt% silica (dmean ∼ 85 nm) particles with 7.5 mM DADMAC were centrifuged as above and the collected supernatants were mixed with 5 ppm of Eosin Y dye (purchased from Alfa Aesar) that is known to bind to DADMAC.21,22 UV-vis spectra of the samples were measured in a quartz cuvette with an optical path length of 1 cm using a Perkin Elmer Lambda 35 UV-Vis spectrometer over the wavelength range of 430 to 580 nm. Spectral absorbance of aqueous solutions containing 5 ppm Eosin Y dye with and without 7.5 mM DADMAC were also measured for reference and used to compare with the spectral data of the supernatants.

Results and Discussion

Fig. 2 shows the measured RRs of PECVD TEOS blanket films as a function of applied down pressure for different concentrations of DADMAC. All the polishing experiments were done at pH 4 where high oxide RRs were reported earlier.10,23,24 The 1 wt% of ceria slurry...
the oxide RRs completely all the way up to 4 psi. Addition of 5 mM DADMAC to the slurry suppressed the RRs over the entire pressure range, but the linear increase with pressure is maintained. However, the straight line representing the data does not pass through the origin anymore, indicating a threshold pressure of around 0.6 psi for the RR to start increasing.

When the DADMAC concentration was increased to 7.5 mM and 10 mM of DADMAC in the slurry, respectively. For all these slurry pressures were around 0.6 psi, 1 psi and 2 psi for 5 mM, 7.5 mM and 15 mM of DADMAC in the slurry, respectively. For all these slurry compositions, RRs still increase linearly beyond the threshold pressure, but at a rate that diminishes with increasing DADMAC concentration. Finally, a further increment of DADMAC concentration to 25 mM suppressed the oxide RRs completely all the way up to 4 psi.

In Fig. 3, the effect of varying the pH of the slurry from 4 to 6 on both TEOS and thermally grown oxide films is shown. For the both the oxide films, RRs showed a similar trend at both pH values, but with much lower RRs for the thermal oxide films, likely due to the relative difference in the film stress and atomic composition. The threshold pressures, ~0.25 psi for pH 6 and ~1 psi for pH 4, are also the more or less the same for the two oxide films.

To better understand these RR data, zeta potentials, TGA and UV-Vis spectra of the ceria particles and the silica particles with and without DADMAC were measured.

**Figure 3.** RRs of SiO2 (TEOS) and thermal oxide (Tox) films as a function of applied down pressure obtained using 7.5 mM DADMAC at pH 4 and pH 6. The dotted lines are obtained by a least square fit of the data and are useful for visualizing.

**Figure 4.** TGA results of silica ((b), (c) and (f) with solid line) and ceria ((a), (c) and (d) with dashed lines) particles for various concentrations of DADMAC.

**Figure 5.** Zeta potential value of 1 wt% silica and ceria particles with and without 25 mM DADMAC at pH 4.

**Table I.** Weight loss (%) of silica and ceria particles centrifuged from DADMAC containing dispersions.

| Conc. of DADMAC | Normalized Weight Loss (%) |
|-----------------|-----------------------------|
| 10 mM           | 0.07                        |
| 50 mM           | 0.8                         |
| 100 mM          | 1.7                         |

**Adsorption strength of DADMAC on SiO2 and CeO2 abrasives.—** The measured zeta potentials of 1 wt% of silica (dmean ≈ 85 nm) and 1 wt% of ceria (dmean ≈ 140 nm) particles both in dispersions without DADMAC are −46.4 mV and +73.5 mV, respectively (Fig. 5). For subsequent measurements, we used 25 mM of DADMAC concentration since, as stated earlier, even at a particle loading of only 1 wt%, the silica particles in the dispersion collectively have a relatively large surface area and consequently, more functional groups than the oxide film surface on an 8″ wafer. Also at this 25 mM concentration, the oxide RR is completely suppressed.

**DADMAC Adsorption on SiO2 and CeO2 Abrasives.—** Fig. 4 shows the TGA data of silica and ceria particles exposed to three concentrations (10, 50 and 100 mM) of DADMAC. Silica particles in 1 wt% silica dispersion containing 10 mM DADMAC showed a slightly larger weight loss than ceria particles in a similar dispersion, though both values are within the experimental sensitivity of the measurements. Increasing the DADMAC concentration to 50 and 100 mM led to higher weight losses (the data are also shown in Table 1), more so for silica than for ceria particles. Thus, one can conclude that more of DADMAC molecules adsorb on silica particles than ceria particles.

Based on these results, it appears that the suppression of the oxide film RRs when DADMAC was added to ceria dispersions is due to the creation of an adsorbed DADMAC layer on the oxide film, since only a negligible amount of DADMAC is adsorbed on ceria particles especially at the lower concentrations used in the polishing experiments. Indeed, this DADMAC layer can prevent the interaction between the oxide surface being polished and the ceria abrasives as suggested by Kang et al.15,16,26 and Shimono et al.23 Also, while the adsorption of DADMAC on ceria particles is low and can be considered weak (see below), it can lower the oxide RRs if it reduces the number of reactive species on the ceria surface.25,27–30

**Adsorption strength of DADMAC on SiO2 and CeO2 abrasives.—** The measured zeta potentials of 1 wt% of silica (dmean ≈ 85 nm) and 1 wt% of ceria (dmean ≈ 140 nm) particles both in dispersions without DADMAC are −46.4 mV and +73.5 mV, respectively (Fig. 5). For subsequent measurements, we used 25 mM of DADMAC concentration since, as stated earlier, even at a particle loading of only 1 wt%, the silica particles in the dispersion collectively have a relatively large surface area and consequently, more functional groups than the oxide film surface on an 8″ wafer. Also at this 25 mM concentration, the oxide RR is completely suppressed.
Interestingly, the addition of 25 mM DADMAC in the dispersion lowered the zeta potential of ceria particles from +73.5 mV to +33.2 mV, in spite of the negligible adsorption and the positive charge on the DADMAC molecules at all pH values. The negligible adsorption of DADMAC implies that a large amount of positively charged free ions (DADMA⁺) remain in the dispersion. These combined with an equal number of Cl⁻ ions dissociated from DADMAC molecules in the dispersion can compress the electrical double layer near the particle surface, resulting in a significant reduction in the range of the electrostatic forces and, hence, a reduction of the zeta potential, similar to the effect of increasing the ionic strength. As shown in Fig. 5, the zeta potential increased after centrifugation and redispersion process. Indeed, just one such centrifugal washing process was sufficient to increase the zeta potential of the redispersed ceria particles to 64.2 mV (all the free DADMAC was washed away), and it remained almost constant after multiple centrifugal washing processes and is very close, within experimental error, to the starting value. These data also demonstrate that the very small amount of DADMAC that was indeed adsorbed on to the ceria surfaces can be desorbed by just one centrifugal washing, suggesting of very weak coupling between them.

In contrast, the zeta potential of silica particles increased from −46.4 to +14.3 mV and remained more or less constant at ~16 mV even after multiple centrifugal washing steps (see Fig. 5), suggesting that DADMAC does not desorb easily from silica surfaces unlike from ceria particles. The adsorption itself is due to the electrostatic interaction between the positively charged DADMAC molecules and the negatively charged silica surface. The charge inversion of the zeta potential of silica particles from negative to positive due to the adsorption of DADMAC molecules occurs via ionic exchange and charge neutralization.

Recently, Penta et al. reported similar results demonstrating strong adsorption of poly-DADMAC (MW: 300–400 kDa) on silica, silicon nitride and poly-Si surfaces, and weak adsorption on ceria surfaces. Thus, it appears that the monomer and the polymer molecules may have similar adsorption characteristics on oxide and the ceria surfaces.

**UV-vis adsorption data.**—The presence of DADMAC in the supernatants of centrifuged ceria and silica dispersions can be quantified using Eosin Y dye which shows a strong absorption peak at 516 nm and whose intensity is lowered when it binds with DADMAC. For example, the absorption peak heights of an aqueous solution containing 5 ppm Eosin Y dye were ~0.54 and ~0.41 (arbitrary units) in the absence and presence of 7.5 mM DADMAC (Fig. 6a and 6d), respectively. These can be compared with the measured peak heights for the supernatants and used to quantify the amount of DADMAC released from the surface of silica and ceria particles into the supernatant. It should be noted that the spectra display a shoulder between 475–490 nm and also the peaks shift in wavelength, presumably due to the complex formed between the dye and DADMAC molecules.

Fig. 6 shows the absorbance in the 516 nm wavelength region for the supernatants obtained from centrifuging 1 wt% silica and 1 wt% ceria dispersions, both containing 7.5 mM DADMAC to which 5 ppm of Eosin Y was added. The peak heights for the supernatant from 1 wt% ceria particles (Fig. 6c) is close to that of the 7.5 mM DADMAC solution (Fig. 6d) and both are considerably lower than that for silica particles (Fig. 6b). Indeed, (Fig. 6b) is very close to that the 5 ppm dye solution (Fig. 6a) containing no DADMAC.

These results suggest that, consistent with our earlier TGA and zeta potential data, almost all of the DADMAC desorbs from the ceria surfaces after centrifugal processing and is released into the supernatant, while most of it remains on silica surfaces. These results are also similar to those of Penta et al. and Trotter et al. who used a centrifugal washing method similar to ours and analyzed the total organic content in the supernatant.

**Proposed mechanism for the observed non-prestonian removal rates.**—Ceria particle dispersions without any additives yield high oxide RRs, as reported by several authors. Several of these authors proposed that the Ce³⁺ species on the surface of ceria particles are responsible for the high oxide RRs by creating strong Ce-O-Si bonds at the surface which cause rupture of the weaker underlying Si-O-Si bonds resulting in material removal during polishing. It has been reported in our earlier publications that silica slurries with additives such as primary amines (amino acids), secondary amines (proline, piperasezine and imizazole) and tertiary amines (pyridine) showed high oxide RRs while suppressing nitride RRs to very low values at 4 psi down pressure. The mechanism of high oxide and low nitride RRs was correlated to the difference in the adsorption behavior of these various additives on the oxide, nitride and ceria surfaces.

Most of these oxide polish rates reported using silica slurries with various additives have a strong pH dependence because of the variation in the extent of pH-dependent protonation and deprotonation of the functional groups in these additives. While the bond formation between the SiO₂ surface and the protonated amino groups of those additives takes place through hydrogen bonding, quaternary ammonium compounds (QACs) or quaternary amines, like DADMAC, can bind differently. Such quaternary amines have a permanent positive charge with a structure R₄N⁺, and, hence, can interact electrostatically with the negative species present on a SiO₂ surface at all pH values as shown in Fig. 7. In fact, Penta et al. showed that PDADMAC, the polymer form of DADMAC, adsorbs on a silica surface primarily due
to the electrostatic attraction between the negatively charged oxide surface and the positively charged PDADMAC at all pH values in the range of 2 to 12.

Increasing the pH of the slurry also increases the reactive species present on the surface of ceria particles.\textsuperscript{23,24} Since the oxide film RR is proportional to the amount of reactive species,\textsuperscript{23,24} the RR of the oxide film increases by increasing the pH in the case of DADMAC, as shown in Fig. 3, despite the stronger bond between it and the oxide film at the higher pH regions.

When the electrostatic interaction between silica and DADMAC is strong enough to form a strongly adsorbed layer on the silica surface, it can suppress the RR of the underlying oxide film. A similar suppression of the RR of both oxide and nitride films was reported by Penta et al.\textsuperscript{25} using 250 ppm PDADMAC who suggested that since the strength of the bridging attraction between PDADMAC and both the oxide and nitride films is weaker than the strength of the underlying Si-O and Si-N bonds, removal of the underlying film is not favored. This suggestion can also explain the suppression of the oxide RRs when DADMAC is added to the slurry. Furthermore, as shown in Fig. 2, the extent of suppression increases with increasing concentration of DADMAC in the slurry, requiring increasingly higher pressures to initiate removal. When the concentration reaches 25 mM, there is no removal even at 4 psi, likely due to the formation of thicker and dense layer on the film surface.

**Effect of applied down pressure on the polishing mechanism.**

The RR of the oxide film for different concentrations of DADMAC was shown in Fig. 2 as a function of applied down pressure. When the applied pressure is low, the abrasive particles are likely prevented from contacting the wafer surface by the adsorbed DADMAC layer, as shown schematically in Fig. 8, making the so-called “chemical tooth” mechanism\textsuperscript{58} inoperative. The schematic in Fig. 8 is consistent with the Zeta potential, TGA and UV-vis spectral data which showed that DADMAC binds only weakly with ceria particles but strongly with the oxide particles and that the adsorbed amount on the oxide particles increases with the concentration of DADMAC. When the applied pressure is increased, while maintaining the concentration of DADMAC, the ceria particles can penetrate through the adsorbed DADMAC layer and contact the oxide film surface. This is similar to the suggestion of Kang et al.\textsuperscript{13,14,15} and Shimono et al.\textsuperscript{26}

**Conclusions**

A ceria-based slurry containing DADMAC (a cationic additive) showed non-Prestonian RR dependence on pressure while polishing TEOS and thermal oxide films at pH 4. For example, when the 1 wt% ceria dispersion contained 15 mM DADMAC, the TEOS oxide film RR was completely suppressed at 1 and 2 psi applied pressures and increased linearly at higher pressures and with 25 mM DADMAC, the rate was similarly suppressed even at 4 psi. This particular non-Prestonian ceria-based slurry has a considerably lower threshold pressure for oxide removal compared with those reported earlier.\textsuperscript{15,16,47} Thermal oxide films also have more or the less the same threshold behavior but the RRs at higher pressures are lower.

TGA and UV-Vis spectral data showed that more DADMAC molecules are adsorbed on silica particles (as oxide film representative) than on ceria particles, while the zeta potential data showed that the binding strength between DADMAC and silica is much higher than that with ceria surfaces. Thus, the more strongly adsorbed DADMAC layer on the oxide surface can resist the ceria particles from contacting the oxide surface till the applied pressure exceeds a threshold value that increases with increasing DADMAC concentration. Beyond this threshold pressure, the film RR increases linearly. The testing of this slurry on patterned STI structures still needs to be performed to evaluate its usefulness for lowering dishing.

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**References**

1. F. Jakubowski, P. Baars, and J. S. Rudecker, U.S. Pat. No. 8,415, 214 (2013).
2. S. Siddiqui, M. M. Chowdhury, M. Brodsky, N. Rahim, M. Dai, S. Krishnan, S. Figuara, E. Wu, A. Chou, and S. Narasimha, ECS Transactions, 53, 3 (2013).
3. M. Krishnan, J. W. Nalaskowski, and L. M. Cook, Chem. Rev., 110, 1 (2009).
4. M. Blumenstock, J. Theisen, P. Pan, J. Dalak, A. Ticknor, and T. Sandwick, Journal of Vacuum Science & Technology B: Microelectronics and Nanometer Structures, 12, 1 (1994).
5. J. Jin, S. Lin, and H. Hocheng, J. Electrochem. Soc., 152, 8 (2005).
6. T. Hoshino, Y. Kurata, Y. Terasaki, and K. Susa, J. Electrochem. Soc., 150, 11 (2003).
7. Q. Luo, S. Ramarajan, and S. Babu, Thin Solid Films, 335, 1 (1998).
8. J. Steigerwald, S. Murarka, R. Gutmann, D. Duquette, and D. Mater. Chem. Phys., 41, 3 (1995).
9. S. Sivaram, H. Bath, E. Lee, R. Leggett, and R. Tolles, Tech. Rep., Sematech, Austin, TX, (1992).
10. Y. Kim, Y. Jung, G. S. Yoon, J. Moon, A. Watanabe, M. Naito, and U. Paik, Journal of Nontronite Science and Nanotechnology, 12, 3 (2012).
11. D. Boning, B. Lee, C. Oji, D. Onuma, T. Park, T. Smith, and T. Tugbawa, Materials Research Society Symposium Proceedings, 566, 197 Warrendale, Pa (1999).
12. H. Van Kraneburg and P. Woerlee, J. Electrochem. Soc., 145, 4 (1998).
13. D. Huang, S. Babu, L. Wang, and T. Moser, ECS Transactions, 33, 10 (2010).
14. H. Nojo, M. Kodera, and R. Nakata, Electron Devices Meeting, 349 (1996).
15. H. Kang, T. Katoh, H. Park, U. Paik, and J. Park, Journal of Applied Physics, 44, (2005).
16. H. Kang, D. Kim, T. Katoh, S. Kim, U. Paik, and J. Park, Japanese Journal of Applied Physics 45, (2006).
17. T. Katoh, M. Kim, U. Paik, and J. Park, Japanese Journal of Applied Physics, 43, (2004).
18. L. Wang, B. Liu, Z. Song, W. Liu, S. Feng, D. Huang, and S. Babu, Electrochemical and Solid-State Letters, 14, 3 (2011).
19. N. K. Penta, B. Peethala, H. Anamapu, A. Melman, and S. Babu, Colloids Surf. Physicochem. Eng. Aspects (2013).
20. S. Francis, L. Vardasney, D. Mitra, and S. Sahabruw, J. Appl. Polym. Sci., 111, 2 (2009).
21. H. Hong, G. Yoo, J. Choi, and J. Taylor & J. Francis (1999).
22. N. K. Penta, J. B. Matovu, P. Veera, S. Krishnan, and S. Babu, Colloids Surf. Physicochem. Eng. Aspects, 388, 1 (2011).
23. P. V. Dantu, B. Peethala, and S. Babu, J. Electrochem. Soc., 157, 9 (2010).
24. P. D. Veera, P. Peddetti, and S. Babu, J. Electrochem. Soc., 156, 12 (2009).
25. W. Tseng, Y. Wang, and J. Chin, J. Electrochem. Soc., 146, 11 (1999).
26. N. Shimono, N. Koyama, and M. Kawaguchi, Japanese Journal of Applied Physics, 45, 4196 (2006).
27. P. Veera Dantu, V. Devarapalli, and S. Babu, J. Colloid Interface Sci., 347, 2 (2010).
28. R. Manivannan and S. Ramanathan, Appl. Surf. Sci., 255, 6 (2009).
29. R. Sabia and H. J. Stevens, Mack. Sci. Technol., 4, 2 (2000).
30. A. Kelsall, Glass Technol., 39, 1 (1998).
31. N. K. Penta, P. Dantu Veera, and S. Babu, Langmuir, 27, 7 (2011).
32. N. Dimov, V. Kolev, P. Kralchevsky, L. Lyutov, G. Broze, and A. Mehreteab, J. Appl Polym Sci, 152, 1 (2009).
33. M. Elimelech, W. H. Chen, and J. J. Waypa, Colloid Interface Sci., 197 Warrendale, Pa (1999).
34. R. Sabia and H. J. Stevens, Glass Technol., 39, 1 (1998).
35. H. Jenny and R. Reitermeier, J. Phys. Chem., 39, 5 (1935).
36. H. Trottler, A. A. Zaman, and R. Parth, J. Colloid Interface Sci., 286, 1 (2005).
37. T. Hoshino, Y. Kurata, V. Terasaki, and K. Sasa, J. Non Cryst. Solids, 283, 1 (2001).
38. L. M. Cook, *J. Non Cryst. Solids*, **120**, 1 (1990).
39. W. G. America and S. Babu, *Electrochemical and Solid-State Letters*, **7**, 12 (2004).
40. M. Boumahraz, V. Y. Davydov, and A. Kiselev, *Chromatographia* **15**, 12 (1982).
41. A. A. Tsyganenko and E. A. Trusov, *Colloid J.*, **40**, 875 (1978).
42. A. Tsyganenko, E. Storozheva, O. Manislova, T. Lesage, M. Daturi, and J. Lavallely, *Catalysis Letters*, **70**, 3 (2000).
43. B. Granqvist, T. Sandberg, and M. Hotokka, *J. Colloid Interface Sci.*, **310**, 2 (2007).
44. L. Zhuravlev, *Colloids Surf. Physicochem. Eng. Aspects* **173**, 1 (2000).
45. Y. Homma, T. Masuda, J. Nair, and J. Shen, *International Conference on Planarization/CMP Technology*, **35** (2009).
46. H. Kang, T. Kato, W. Lee, U. Paik, and J. Park, *Japanese Journal of Applied Physics* **43**, 1A (2004).
47. Y. Kim, J. Kim, A. Watanabe, M. Naito, and U. Paik, *Electrochemical and Solid-State Letters* **12**, 12 (2009).