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ORIGINAL PAPER

An investigation of phosphate based ECMP electrolyte performance on feature scale planarization

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Abstract Conventional copper chemical mechanical planarization (CMP) techniques are being pushed to their limits by increasing industrial standards caused by device miniaturization and the use of new materials. There is a need to investigate alternative methods of polishing to maintain and/or improve planarization standards while operating at low downforce. In this study, electrochemical mechanical planarization (ECMP) is considered as an alternative and/or an extension to current CMP processes. ECMP is unique due to the combination of an applied voltage to oxidize Cu and an abrasion from a polishing pad, which potentially allows the system to achieve high levels of planarization through the use of an appropriately tailored electrolyte. An electrolyte containing 1.0 M potassium phosphate salt concentration with a pH value of 2 and a benzotriazole (BTA) concentration of 0.001 M was tested for its planarization capability on patterned Cu structures using a custom built ECMP tool. Feature sizes of the Cu structures were varied from 1 to 6 μm. Similar planarization results were achieved using three pad types. All experiments were performed at 0.5 V versus Ag/AgCl reference. The average step height reduction (SHR) was ~840 nm while the decrease in the average metal thickness removed (λ_{avg}) was on the order of ~430 nm. Because features were approximately 50% of the substrate area, the total average metal thickness removed was approximately half of the SHR for all three pad types.

Keywords Copper · ECMP · BTA · Planarization · Potassium phosphate

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1 Introduction

The planarization of Cu interconnects is challenging due to decreased feature sizes with increased packing densities, more intricate surface topographies, a growing number of interconnect layers, and the introduction of low-k dielectric materials [1–3]. Chemical mechanical planarization (CMP) is presently the leading technology employed for leveling Cu damascene structures during the fabrication of ICs [4, 5]. However, conventional CMP processes are limited when addressing new challenges due to the use of abrasive slurry particles and strong downforce required to achieve planarization [6–8]. In addition to anticipated CMP limitations, there exists a strong demand to meet industrial standards to achieve higher planarization efficacy, while causing less defects (i.e., dishing, erosion, delamination), and attaining higher throughputs at lower downforce [3, 6, 8, 9].

Electrochemical polishing (ECP) and electrochemical mechanical planarization (ECMP) have emerged to offer alternative means of planarization, due to their potential improvements in both the reduction of consumables use and the increase in planarization performance compared to current technologies [9–11]. However, recent studies have shown that the use of ECP alone will not suffice for future nodes, especially for planarization of low-aspect ratio features [5]. ECMP could be used as an extension or possible replacement to current CMP processes, though the removal mechanism, which is thought to be the key to its superior planarization efficiency, has not been comprehensively studied or characterized [6].

ECMP exploits the combined effect of the anodic dissolution of a metal via an applied voltage and the delicate abrasion of the sample surface from a polishing pad. The use of an applied voltage causes Cu oxidation to occur

without the use of oxidizing agents present in the electrolyte. Therefore, ECMP may not require strong oxidizers and/or abrasive slurry particles, which are known to contribute significantly to surface defectivity during the planarization process [9, 10, 12]. To quantify planarization capability of an ECMP electrolyte using a rotating disk electrode (RDE) on a simplified feature (Fig. 1a), we used a planarization factor, ε, defined in a previous paper as:

$$\varepsilon = \frac{s_o - s_f}{\lambda_{avg}} \quad (1)$$

where λ_{avg} is the average metal thickness removed, s_o is the initial step height before planarization and s_f is the final step height of the feature after planarization [13]. As ε increases, feature scale planarization increases. Equation 1 was used to predict planarization capabilities of ECMP electrolytes using electrochemical methods on both a custom built bench top ECMP tool, using blanket wafer fragments, and a Cu RDE [11]. The optimized ECMP electrolyte from the previous study is currently being used in this study to focus on the actual planarization of various patterned structures. Tripathi et al. performed planarization studies with an ECMP electrolyte utilizing 5-phenyl-1-H-tetrazole (PTA), hydroxyethylidenediphosphoric acid (HEDP), and oxalic acid; however planarization on patterned structures was only demonstrated with the use of abrasive particles [14].

Figure 1b illustrates a proposed Cu removal mechanism for ECMP using BTA as an inhibitor. It is known that in general, there are at least two possible types of film that BTA can form on a Cu surface. A BTA inhibition layer can either be formed by chemisorption of Cu and BTA in the form of Cu:(BTAH)^{ad} or the formation of a polymeric

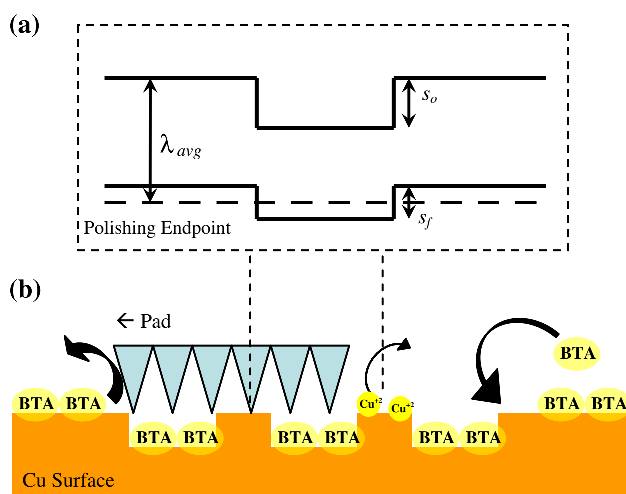

Fig. 1 **a** Simplified trench schematic diagram showing an idealized topography with an initial feature with step height s_o. After ECMP has removed λ_{avg} of Cu film, the final step height is assumed to be s_f. **b** Proposed BTA removal mechanism

BTA–Cu complex film over the Cu surface [15, 16]. In acidic environments, BTAH is preferentially protonated, leaving the BTA to form a chemisorbed species on the Cu surface rather than the polymeric Cu–BTA complex [16]. The adsorbed Cu:(BTAH)^{ad} complex is still able to protect the Cu from electrochemical dissolution, though it is not as effective as the polymeric complex [15]. Figure 1b shows an illustration of the BTA adsorbed onto the Cu surface. This protective film, being lightly attached to the Cu, can be easily removed by slight abrasion from a polishing pad. In acidic environments, since protonation decreases the energy of the π orbital, there is lower resonance energy between BTA and Cu, therefore causing a weaker interaction between the two species [16]. Once the pad has passed over the surface, the BTA protective layer begins to reform over the freshly dissolved Cu surface, as seen in Fig. 1b. This could be the reason that ECMP can potentially operate at significantly low downforce. Similarly to CMP processing, post ECMP cleaning is likely to be necessary for the removal of potential BTA residue present after polishing.

This study is intended to explore the planarization capability of a phosphate based electrolyte containing BTA as an additive, as a validation of a previous ECMP electrolyte screening study [11]. Operating potential and other characteristics of this electrolyte have been previously examined and the optimized set of electrolyte characteristics and operating conditions are used throughout this investigation [11]. A custom built ECMP tool was employed to perform experiments using wafer samples with a patterned Cu structure and planarization results are shown. Based on these results, future electrolyte development and optimization can be considered.

2 Experimental

All RDE electrochemical experiments were performed at room temperature with a standard three electrode setup using a Cu working electrode (WE) (area = 0.196 cm^2, purity = 99.9%), Pt wire counter (CE), and a saturated Ag/AgCl reference electrode (REF). The working electrode was hand polished with 600 grit sandpaper and thoroughly rinsed with de-ionized (DI) water before every experiment. Experiments were carried out using a μAUTOLAB Type III potentiostat and a variable speed four contact rotator (Pine Instrument Co. AFMSRX). Potentiodynamic experiments were scanned from −0.5 to 3.0 V versus Ag/AgCl reference at a rate of 5 mV s^{-1} with a rotation speed of 100 rpm.

The electrolyte was prepared using ortho-phosphoric acid (85%, Fisher), potassium phosphate (monobasic, Fisher), benzotriazole (Fisher), and de-ionized (DI) water. All

solutions were prepared as 1.0 M potassium phosphate and adjusted to a pH value of 2 using small amounts of phosphoric acid, unless otherwise noted. We would like to point out that the addition of phosphoric acid does slightly increase the overall phosphate concentration within the electrolyte. The inhibitor BTA was used in a concentration of 0.001 M during all planarization experiments and other concentrations were noted for RDE experiments. Average surface roughness (not shown) and step height analysis results were obtained with an Alpha-Step IQ KLA Tencor Profilometer.

ECMP results were performed on a custom built tool shown in Fig. 2. The tool operates in two dimensional linear motion, where the wafer is mounted parallel above a nonconductive CMP pad which has holes punched out that occupy 50% of its area. The wafer sample is lowered onto the polishing pad and movement occurs from left to right, a distance of ~6 cm across the length of the pad, at ~70 cycles per minute with a slight 1 mm offset motion. Electrical contact is made to the wafer surface (anode) via Cu foil and an Ag/AgCl reference and a Cu counter (cathode) electrode are located within the electrolyte bath. The tool is operated at approximately 1 psi. A more detailed description of the tool can be found in a previous paper [11]. The tool is operated using an E.G&G Princeton Applied Research Potentiostat/Galvanostat Model 273A at an applied potential of 0.5 V versus Ag/AgCl reference.

Patterned structures were fabricated through a series of electrochemical plating (EP) and electrochemical polishing (ECP) steps. Wafer samples were plated with copper on a preexisting copper seed layer (~100 nm thick) using a plating bath consisting of 240 mM cupric sulfate ($CuSO_4$), 1.8 M sulfuric acid (H_2SO_4), 5 ppm of bis 3-sulfopropyl-disulfide (SPS), 300 ppm of polyethylene glycol (PEG) and 50 ppm of chloride ions (Cl^-) in the form of hydrochloric acid (HCl) [17]. Samples were typically plated at a rate of 10 mA cm^{-2} up to thicknesses between 5 and 10 μm. After electroplating, samples were patterned with lithography. Patterns consisted of 5 consecutive lines and spaces with separation of ~200 μm (Fig. 3a, b). Once these patterns were made, the samples were electropolished in phosphoric acid at constant potential of 1.2 V [18]. Polishing time was varied according to the desired depth of the features. Trench height varied from 1 to 6 μm, depending on the time of dissolution. Following electropolishing, sample roughness and thickness were recorded to monitor changes caused by planarization. It should be noted that due to variations in current density distribution, the trenches were not uniform as shown in the profilometric scans. This edge effect is not caused by the ECMP process.

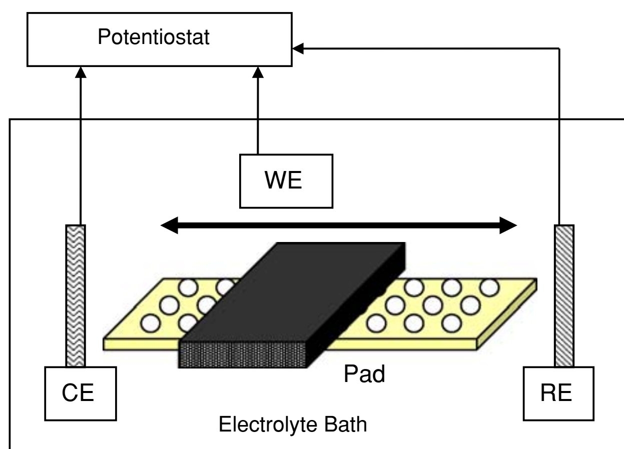

Fig. 2 ECMP tool schematic (*side view*). The WE is a wafer fragment mounted on a platen that moves linearly in the two dimensions parallel to the pad. This platen is lowered onto a platform that has a pad mounted on a perforated support. To complete the circuit a Cu CE is placed within the bath, as well as an Ag/AgCl RE. The pad contains holes that account for 50% of the pad's surface area

3 Results and discussion

Previous work has shown that a RDE is an efficient tool to screen electrolytes [11]. Figure 4a shows a summary of results of a phosphate based electrolyte screening process where an optimal electrolyte was found. In concentrated phosphoric acid, the presence of BTA, even at a concentration an order of magnitude higher than that in a pH value of 2, has little effect on the polarization curve. Due to the

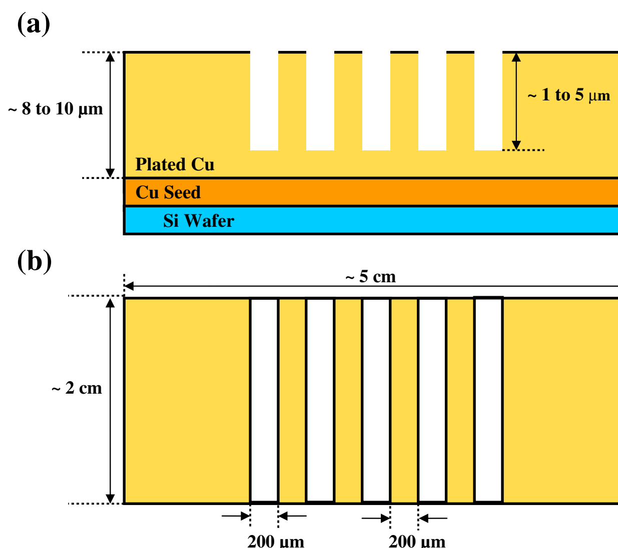

Fig. 3 **a** *Side view* of the patterned structure created through EP and ECP. The trenches can vary in depth from 1 to 6 μm. The presence of the Cu seed layer and the barrier material are also shown in this illustration. **b** *Top view* of the feature pattern that includes five trenches each spaced 200 μm from one another, each also with a width of 200 μm

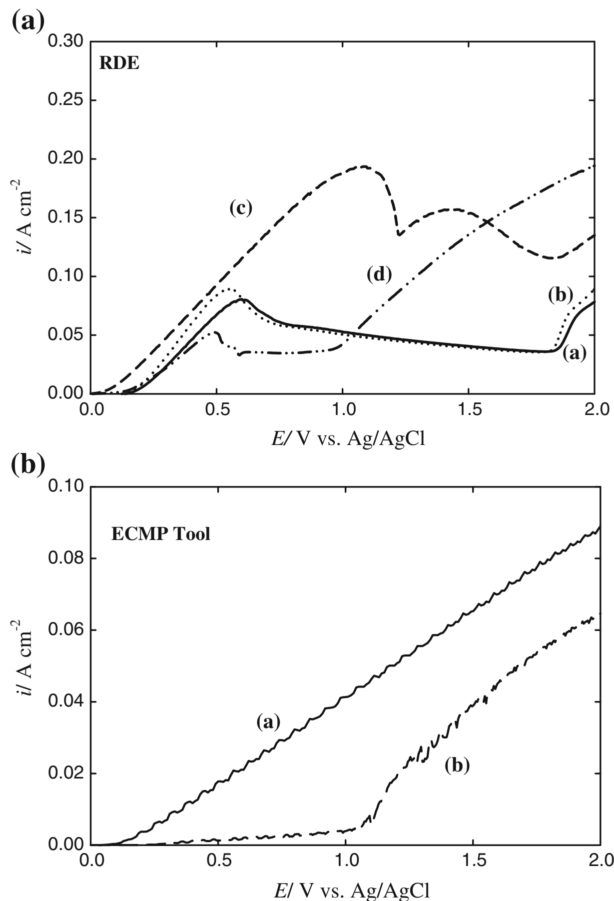

Fig. 4 **a** Anodic polarization for oxidation of a Cu RDE with a rotation speed of 100 rpm. *Curves a* and *b* are electrolytes of concentrated phosphoric acid (pH ~0) containing: (*a*) $c_{BTA} = 0$, (*b*) $c_{BTA} = 0.01$ M. *Curves c* and *d* are electrolytes containing 1.0 M potassium phosphate salt at a pH value of 2 containing: (*c*) $c_{BTA} = 0.0$ M, (*d*) $c_{BTA} = 0.001$ M. **b** Anodic polarization for oxidation of a Cu wafer on the ECMP tool operating without pad contact. Electrolytes containing 1.0 M potassium phosphate salt at a pH value of 2 containing: (*a*) $c_{BTA} = 0.0$ M, (*b*) $c_{BTA} = 0.001$ M

lack of Cu dissolution inhibition, it would not be possible to planarize a Cu sample. Also, because of the viscosity difference between concentrated phosphoric acid and the potassium phosphate solution, phosphoric acid has a considerably lower current density throughout the whole scan than that of the electrolyte with a pH value of 2 [19]. The optimal chemistry shown by a previous study contains a 1.0 M salt concentration with a pH value of 2 with a BTA concentration as low as 0.001 M [11].

Previous results also indicate that BTA can inhibit the dissolution of Cu in an operating potential window from 0.5 to 1.0 V versus Ag/AgCl [11]. Figure 4b demonstrates that with and without BTA present in a 1.0 M potassium phosphate solution with a pH value of 2, at the same concentration (0.001 M BTA) as used during RDE experiments, Cu inhibition is more significant on wafer samples operated on the ECMP tool. The curves labeled a and b in Fig. 4b were performed on blanket wafers both operating with no pad contact. Using this information, the conditions used for all planarization experiments in this study were set to an applied potential of 0.5 V versus Ag/AgCl, using an electrolyte containing 1.0 M salt concentration at a pH value of 2 with a BTA concentration of 0.001 M. This chemistry has demonstrated that in a specific electrical potential region, both good passivation at low inhibitor concentrations and high removal rates can be achieved; additionally with its simplified bath chemistry, this electrolyte offers significant advantage over previous ECMP electrolytes studied.

To demonstrate planarization capability, patterned structures were tested on the ECMP tool. Figure 5 illustrates a control sample polished at a potential of 0.5 V with an electrolyte containing no BTA. The average metal thickness removed (λ_{avg}), as determined by weight loss measurements, was ~500 nm. As seen from Fig. 5, before and after profilometric scans are shown superimposed onto on another and both are nearly identical, indicating little to no step height reduction (SHR) even though there was metal removed from the sample. Without BTA present in the electrolyte, planarization at a pH value of 2 cannot be achieved. Significant roughening from pad contact or the electrolyte did not occur, consistent with results of a previous study [11].

Figure 6 shows planarization results using three different pad types. All pads were nonconductive and 5 mm diameter holes were punched out of each pad; the holes accounted for ~50% of the pad's surface area. All samples (Fig. 6a–c) were performed at an operating potential of 0.5 V with an applied pressure of ~1 psi. Figure 6a shows results obtained by polishing with a Suba^{TM} pad; a SHR of

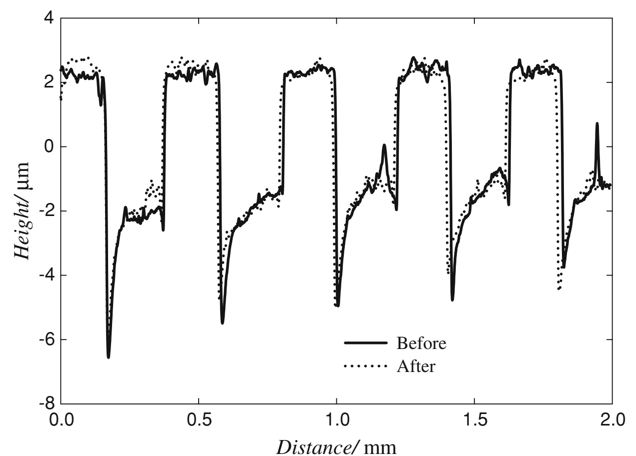

Fig. 5 Profilometry scan of a patterned wafer after polishing with a Suba^{TM} pad for 60 s with an electrolyte containing 1.0 M potassium phosphate salt at a pH value of 2 with no BTA at 0.5 V versus Ag/AgCl

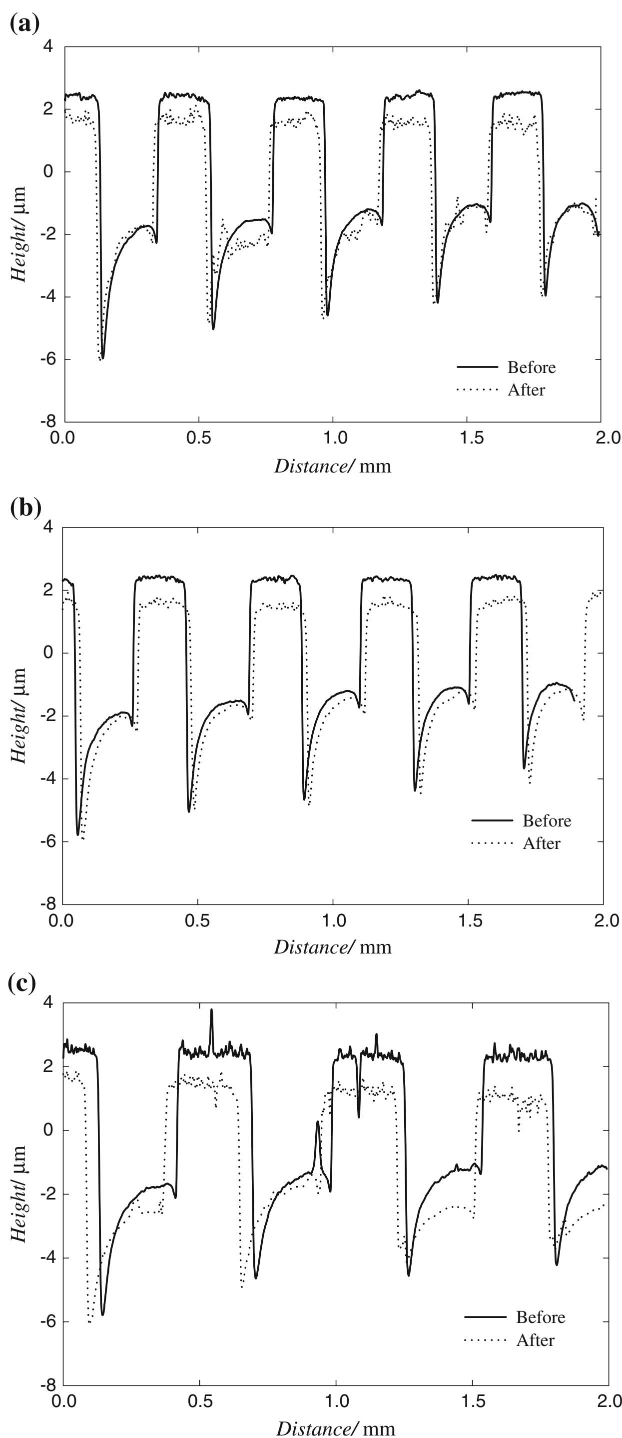

Fig. 6 **a** Profilometry scan of a patterned wafer surface after polishing with a Suba™ pad for 60 s with an electrolyte containing 1.0 M potassium phosphate salt at a pH value of 2 with 0.001 M BTA at 0.5 V versus Ag/AgCl reference. **b** Profilometry scan of a patterned wafer surface after polishing with an IC1000™ pad for 40 s with an electrolyte containing 1.0 M potassium phosphate salt at a pH value of 2 with a BTA concentration of 0.001 M at 0.5 V versus Ag/AgCl reference. **c** Profilometry scan of a patterned wafer surface after polishing with a D100™ pad for 30 s with an electrolyte containing 1.0 M potassium phosphate salt at a pH value of 2 with a BTA concentration of 0.001 M at 0.5 V versus Ag/AgCl reference

~780 nm was achieved. According to weight loss measurements, the average amount of λ_{avg} was ~390 nm. The area used to calculate the amount of material removed was the pad area (including area of holes) in contact with the wafer. There were no added oxidizers to the electrolyte that may etch the Cu at open circuit potential (OCP), therefore leading to dishing and erosion. Our studies have indicated that when there is no potential applied to the wafer surface, little to no removal of Cu can be detected post ECMP when operating with pad contact. When 0.5 V is applied during operation with no pad contact during ECMP, there is also little to no detection of Cu removal. Therefore, consistent with Shattuck et al., it was assumed that on regions with no pad contact there was minimal Cu dissolution [11].

Figure 6b shows results from a similar experiment, where planarization was achieved using the IC1000™ pad. The λ_{avg} during the experiment was ~340 nm, while the actual SHR was ~740 nm. Similarly, Fig. 6c shows planarization achieved using a D100™ pad. The λ_{avg} was ~560 nm and the SHR was ~1,000 nm. In all three cases, similar SHR and λ_{avg} was achieved. The superimposed images exhibit a significant difference post ECMP, in only the area where the pad had contact i.e., the top surfaces of the feature. This could indicate planarization ability and control because of the decrease in SHR due to the selective dissolution of the top features versus the recessed features seen in Fig. 6a–c. However, trials on more complex features in a more controlled environment are necessary to fully support and conclude absolute planarization capabilities using these pads and this electrolyte.

Seen in Fig. 7, a 1 µm sized single trenched structure was created via electrochemical polishing. Post ECMP using a Suba™ pad, seen in Fig. 7, the average metal thickness

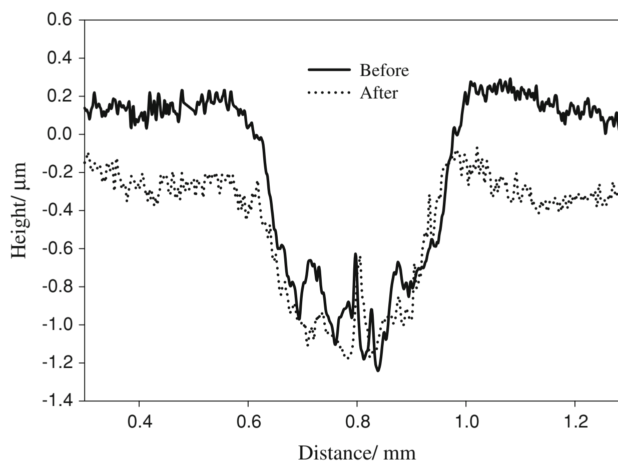

Fig. 7 Profilometry scan of a patterned wafer surface, containing a single trench 1 µm deep, after polishing with a Suba™ pad for 30 s with electrolyte containing 1.0 M potassium phosphate salt at a pH value of 2 with a BTA concentration of 0.001 M at 0.5 V versus Ag/AgCl reference

removed was ∼320 nm with a SHR of ∼400 nm. Due to the difference in feature density from the previous experiments (here, the recessed feature represents ∼2.5% of the total area); there is considerably less difference between the average metal thickness removed and the SHR. We think that there is minimal dissolution of Cu due to the presence of BTA, except in the regions of pad contact which is represented by results in both Figs. 6 and 7.

4 Conclusions

Planarization was achieved on patterned Cu structures with an abrasive-free electrolyte using ECMP. Results indicated that using a low pH phosphate based electrolyte and benzotriazole, as an inhibitor, ECMP can provide the necessary metal removal rate to polish Cu in CMP time constraints, while providing adequate passivation in the recessed regions to allow for planarization to occur. Previous work utilized an electrochemical screening process to determine optimal ECMP electrolyte chemistry and operating conditions. This process was confirmed to be valuable as a screening tool by the results presented above. A step height reduction of approximately 1 μm was achieved using three different pad types. Additionally, pattern densities and trench depths were varied to confirm consistency in polishing results.

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