Environmental Effects on Post-CMP PVAc Brush Releasable Contamination and Break-In Optimization for Advanced Logic and Memory Technologies

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Advanced sub-7nm logic and VNAND memory technologies are becoming more reliant on Chemical Mechanical Planarization (CMP). New layers and materials are being introduced with each new technology node and integration scheme. Polyvinyl-acetal (PVAc) brushes are used extensively for post-CMP contact cleaning and remain the most reliable method for efficient cleaning of slurry residues while minimizing physical damage to sensitive films and structures. The releasable contamination from the virgin PVAc brush, however, is becoming more of an issue with each new technology node often affecting the yield of the device being manufactured. As a result, users are required to "break-in" or pre-condition brushes much longer than before to meet the required defect performance for these technologies. Longer PVAc brush break-in times negatively impact CMP tool utilization and overall equipment efficiency (OEE). This work attempts to characterize PVAc brush releasable contamination sources under simulated post-CMP cleaning conditions and suggests ways to reduce the break-in burden. Liquid particles (LPCs) were analyzed in the brush effluent and samples were subsequently dried and characterized by Fourier-transform infrared spectroscopy (FTIR). Environmental effects such as brush handling, temperature cycling, and dehydration, as well as post-CMP chemistry acclimation were all deemed significant contributors to the final releasable contamination profile and break-in characteristics of the brush. The brush Pore Templating Agent (PTA) represented the largest contribution of particles early in the brush lifetime. Loose PVAc particles were also a significant source of brush releasable contamination. PTA residue appears to decreases rapidly during brush use, whereas PVAc particulates reduce at a slower rate and eventually become the primary source of liquid particles. The physical nature of the post-CMP process and surface changes observed on the brush nodule are evidence that PVAc particulate reduction is largely unavoidable. PVAc brush break-in times, nevertheless, were accelerated by more aggressive break-in conditions and the application of chemistries known to improve the hydrolysis and removal of PTA. Offline but onsite PVAc brush break-in may be the most effective way to recover CMP tool utilization while minimizing environmental and chemistry acclimation effects simultaneously.

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For any contact cleaning application, the user must be cognizant of both the removal efficiency of the cleaning material as well as any potential cross contamination introduced by the cleaning material itself. Polyvinyl-acetal (PVAc) foam brushes used for post-CMP cleaning are no exception. Papers have been published highlighting the effect of PVAc brush cross-contamination on wafer defect levels.[1,2]

Releasable impurities from the brush may be soluble or insoluble. Solid raw materials used to manufacture the PVAc brush are organic and can be both soluble and insoluble in water, depending on the temperature of the reactive mixture used to form the brushes. Most commercially available PVAc brushes used for post-CMP cleaning incorporate a semi-soluble Pore Templating Agent (PTA) in the manufacturing process to systematically create the pore structure (porosity) of the material. The pore structure is necessary to enable fluid transport through the polymeric foam as well as provide the compliancy (softness) necessary for contact on sensitive semiconductor materials. The pore templating agent can take various forms, but are commonly starches processed from either potatoes, corn, wheat, or rice. Starches may be natural or structurally modified to improve their functional characteristics.[3] The pore templating agent of choice, however, should be removed after the brush is polymerized, since it serves no additional purpose for the PVAc foam or its application.

Some information has suggested that impurities from the PVAc brush are predominantly inorganic in nature.[4] For some polymeric foaming technologies, defoaming agents are added to control the formation and dispersion of unwanted foaming in batch processing systems. Silicone-based (e.g. polydimethylsiloxane) defoaming agents are polymers with silicon backbones. These silicon-based chemistries are very commonly used in industrial applications. Alternative (e.g. water-based) defoaming agents exist for both aqueous and non-aqueous environments, but most PVAc foam suppliers have developed processes that do not incorporate defoaming agents at any level.

Aside from potential inorganic manufacturing-related debris, most of the known potential releasable contamination from the PVAc brush is organic. PVAc is a relatively tough material; however, to maintain its compliancy and softness, the material is partially crosslinked. The degree-of-crosslinking (DOC) for PVAc used in the semiconductor industry can vary but is typically on the order of 25–50%. Loose, weakly bonded polymeric chains, perhaps insufficiently crosslinked, render the material susceptible to some degree of natural abrasion from the surface of the brush during the post-CMP process. Other organic or inorganic debris sources could include batch making and fluid handling systems, molds, and tooling in contact with or within close proximity of the PVAc brush in production.

Although a pristine, (releasable) contamination-free PVAc brush desired, this is usually not the case in practice. Depending on the post-CMP application and technology node, the brushes must be conditioned, or broken-in, on post-CMP systems to remove residual organic process debris. The length of brush conditioning depends heavily on the defect tolerance of post-CMP application, with more advanced technology nodes being less tolerant to organic particle contamination; hence requiring longer break-in times. The cost of lost wafer production and poor CMP system utilization can be very high. PVAc brush break-in times to reach specific defect requirements for advanced nodes can be best modeled by an inverse power function (Figure 1). Function constants include an environmental coefficient (A), brush break-in efficiency % (B), and PVAc factor (C).

The ability of the PVAc brush manufacturer to sufficiently remove the PTA, control PVAc abrasion effects, and minimize inorganic particle sources from manufacturing are believed to be the primary attributors to brush break-in times under supplier control. Brush break-in efficiency (B) may include specific chemistries or processes (e.g.

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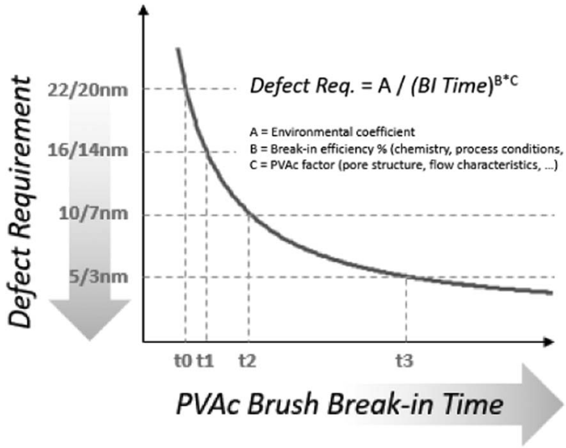

Figure 1. Inverse-power relationship between PVAc brush break-in time and defect requirement.

Figure 2. Cyclone brush processing system.

mechanical or otherwise) used to systematically remove the organic matter in question. The PVAc factor (C) attempts to quantify the physical properties of the material, including but not limited to pore structure, flow characteristics, etc. As expected, more efficient break-in processes and more favorable PVAc properties would reduce break-in times.

In this study, the releasable contamination from the PVAc brush is analyzed as a function of time, and the contribution of organic matter is evaluated. The environmental and handling effects of brush break-in are also investigated by exposing the brush to various conditions common with the transportation, storage, and use/exchange of the PVAc brush. Furthermore, studies were performed to quantify the break-in capability of PVAc brushes under simulated post-CMP conditions, with and without chemistry, in comparison to more aggressive offline conditions.

Experimental

To estimate the PVAc brush environmental effect, brushes were exposed to a few simple conditions to simulate potential PVAc brush conditions during transportation, storage, and handling. The conditions investigated in this study are shown in Table I. This table, however, is not inclusive of all possible transportation and storage effects. Others may include time (polymer aging), material preservation interactions, and UV exposure. After brush exposure, the releasable contamination of the brush was evaluated by dynamic effluent Liquid Particle Count (LPC) monitoring.

To more closely evaluate PVAc brush break-in behavior, brushes were also processed under different conditions and chemical exposures. PVAc brush releasable contamination was quantified by liquid particle detection of the brush effluent during the break-in process. LPC samples were collected at various intervals and the brush effluent was subsequently dried under a heat lamp. The particles obtained after water evaporation were directly analyzed by Fourier-transform infrared spectroscopy (FTIR). Brush motor torque and nodule surface morphology were also characterized by chromatic white light interferometry.

Table I. PVAc brush exposure conditions.

Brush set	Purpose	Condition
1	Brush Handling	Various handling medium/gloves
2	Temperature Cycle	61~97°F, 2 cycles, 48 hrs.
3	Dehydration	Room Temp, ~15% water wt loss, 48 hrs.
4	Vibration	150~200Hz, 2 hrs.

All brushes were processed on ITW Rippey's Cyclone flow through processing system (Figure 2). The Cyclone system is an automated universal brush processing system capable of independently processing all commercially available brush roller formats. The brush speed, deionized water (DIW) flow rate through the mandrel, chemical flow rate, and brush compression into proprietary brush nodule treatment surfaces are all controllable (Figure 3). All DIW and chemistries used were filtered to 0.03μm. The system also incorporates in-line liquid particle counting of the brush effluent, brush motor torque monitoring, and a sample port for offline effluent contamination analysis. LPC detection is performed by a nano65C+ system manufactured by Lighthouse Worldwide Solutions (Sum>65nm).

Results and Discussion

Brush handling during installation into the Cyclone brush process system represented a significant impact on releasable contamination

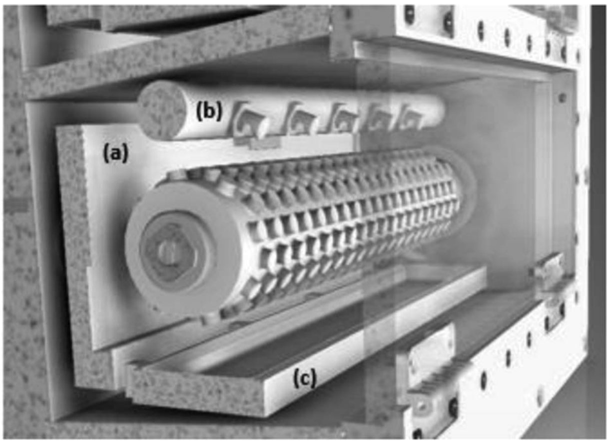

Figure 3. Cyclone PVAc brush chamber with (a) retractable brush conditioning surface, (b) chemical delivery manifold, (c) effluent catch basin.

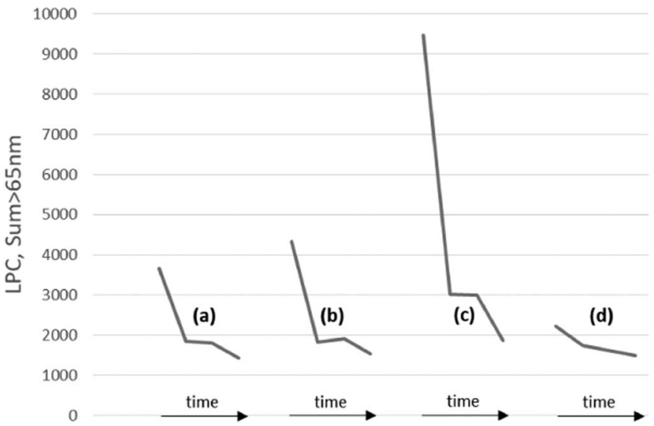

Figure 4. PVAc brush effluent LPC response vs. time under various brush handling conditions (a) without touching PVAc, (b) Class 10 Nitrile CR glove, (c) Powder-free Nitrile LM glove, (d) PVAc wiper.

(Figure 4). Both the glove type and handling method were significant in determining the initial LPC level of the brush and consistent with observations of previous glove studies.[5] Handling the PVAc brush with a PVAc wiper produced the lowest level of releasable contamination. In this case, the PVAc wiper was processed under virtually the same conditions as the PVAc brush itself, reducing the risk of cross-contamination by a foreign material.

The environmental effects due to temperature cycling, dehydration, and vibration are shown in Figure 5. Dehydration of the brush had the most significant impact on LPC levels and break-in performance. Since brushes are typically shipped wet, the moisture content should be carefully controlled. Low Moisture Transmission Rate (MTR) packaging could help; but any condensation as a result of temperature cycling would be unavoidable. Coincidentally, there was significant condensation observed during the temperature cycling test, so the impact of dehydration and temperature cycling are confounding effects. The temperature cycled brushes showed a significantly higher LPC level as well; whereas the brush samples that underwent vibration for 2 hours were within the range of room temperature and moisture controlled samples.

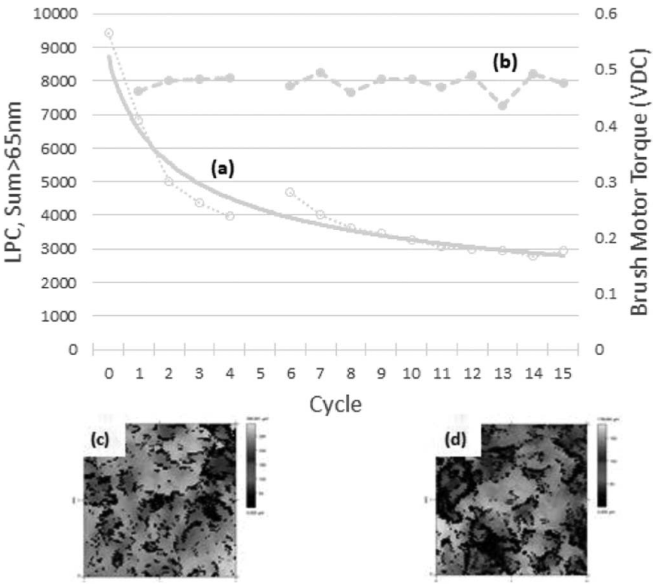

Figure 6. Simulated DIW-only PVAc brush break-in (a) LPC decay, (b) torque trend, (c) PRE-nodule morphology Sa∼10.0μm, (d) POST-nodule morphology Sa∼11.1μm.

For a simulated DIW-only break-in process, the LPC level is high after brush installation and comes down over time. Each cycle represents 20 brush engagements into a quartz conditioning surface at 400RPM, with 1mm compression for 30 seconds (Figure 6). The missing data between cycles 4 and 6 show when the process was idled. Brushes were held moist in the process chamber for approximately 12 hours. Despite a slight increase in LPC counts on restart, the rate of LPC decay follows the inverse-power relationship discussed previously. Eventually, the LPC level appears to reach a point of diminishing returns where there is little change with each new cycle. This LPC power decay is believed to correlate well with PVAc brush break-in behavior and particulate defects on semiconductor wafers with OEM post-CMP equipment.[6] Any substantial decrease in LPCs for longer times would require a change in processing conditions. The brush motor torque was stable over the length of the evaluation period and there was very little observed change in the morphology of the nodule with the DIW-only process.

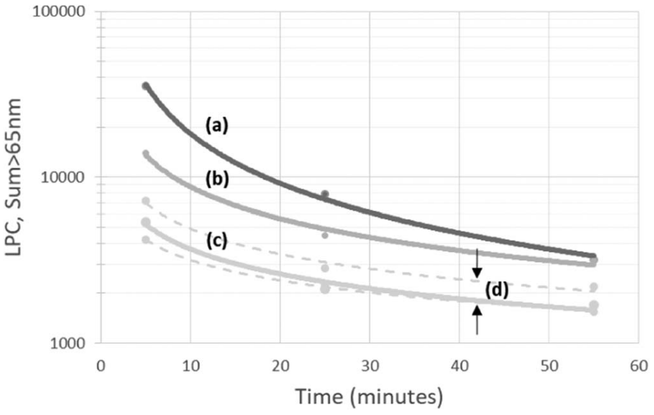

Figure 5. PVAc brush effluent LPC response v. time under various environmental conditions (a) dehydration, (b) temperature cycled, (c) vibration, (d) typical controlled range.

FTIR analysis of the dried PVAc brush effluent showed primarily evidence of PTA, PVAc, and other organic matter attributed to the manufacturing environment of the PVAc brush. Figure 7 shows the FTIR spectrum for brush effluent containing predominantly PTA. The sample is confirmed to be PTA by comparison with reference spectrum for starch. Specifically, the prominent peaks at ∼3380, 2929, 1645, 1366, 1152, 1081, 1025, 934, 852, 763 and 710 cm^{-1} overlap with those of the starch reference, supporting the proposed identification. High resolution optical images of the particles are also shown. Figure 8 shows FTIR spectrum and sample photos for brush effluent containing mostly PVAc particulates. Sample prominent peaks at ∼2915, 2859, 2780, 1734, 1475, 1432, 1407, 1243, 1199, 1003, ∼864

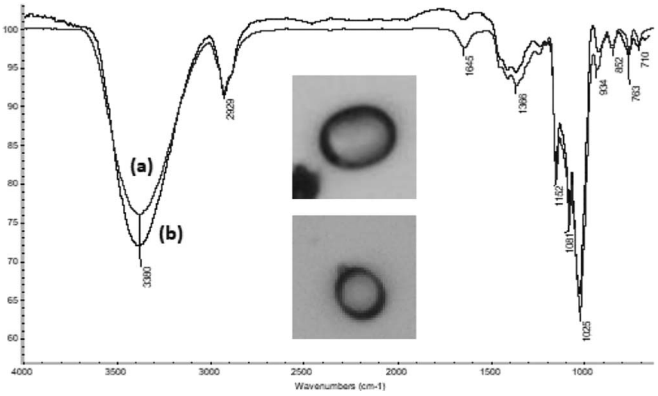

Figure 7. FTIR spectrum for PTA (a) PVAc brush effluent sample, (b) reference.

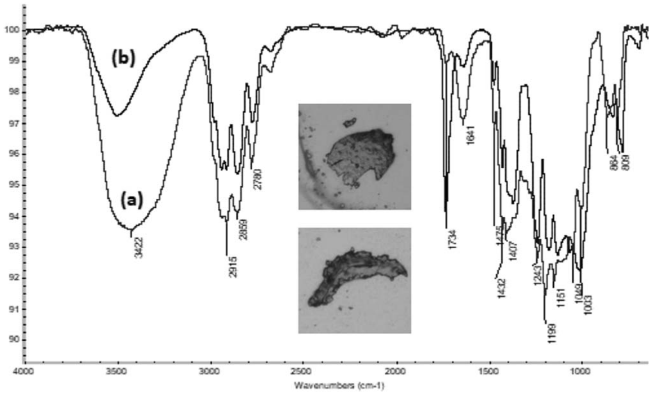

Figure 8. FTIR spectrum for PVAc (a) PVAc brush effluent sample, (b) reference.

and ∼809 cm^{-1} exhibit overlap with those of the polyvinyl acetal reference. Manufacturing-related organic contamination (not shown) consisted primarily of polypropylene, polyvinyl chloride, and trace amounts of polyamide (bacteria).

Effluent samples were collected at four times during the DIW-only break-in process and the level of each primary organic source estimated. Perhaps as expected, PTA represented the highest percentage of organic contamination at the beginning of the break-in process and decreased over time. PVAc was the second highest contributor to LPCs, decreased initially but eventually leveled-off; perhaps as expected given the polymer's DOC and propensity for persistent low levels of polymer chain scission by mechanical forces. Manufacturing-related organic contamination was the lowest percentage, collectively, and also decreased over time (Figure 9). Both PTA and manufacturing-related debris are believed to finite contamination sources, whereas PVAc particulates are not.

The PVAc brush break-in process was also evaluated under alkaline conditions. PVAc brushes were processed in the same manner, but with 250ml of 0.29%wt NH_4OH applied to the brush surface during the break-in process (e.g. when brushes were engaged with the conditioning surface). Compared to the DIW-only process, the LPC rate of decay was improved (greater) and the final LPC level achieved was lower (Figure 10). Brush motor torque remained stable, albeit slightly higher on average than the DIW-only process. The increase in brush motor torque observed is believed to directly correlate to frictional changes at the brush-conditioning surface interface. As a result, the nodule surface was slightly rougher than that of the DIW-only process. The PVAc acclimation effect under these conditions could be related to further (alkaline) hydrolysis of the PTA within the material.[7]

And finally, the PVAc brush break-in process was evaluated under more aggressive, but still alkaline, processing conditions believed to accelerate PTA hydrolysis and PVAc break-in behavior. Aggressive conditions included higher contact pressures, higher speeds, and more efficient absorption of chemistry not capable on post-CMP cleaning systems. The process time (cycle count) and chemical flow rate, however, were kept constant. As expected, LPC decay was improved further under these "optimized" conditions indicating the importance of proper chemical acclimation of the porous polymeric material (Figure 11). The torque remained stable and the nodule surface morphology revealed the largest change (e.g. increase in roughness). Depending on the final brush releasable contamination target, optimizing the PVAc brush break-in process could significantly reduce brush break-in times and chemistry consumed.

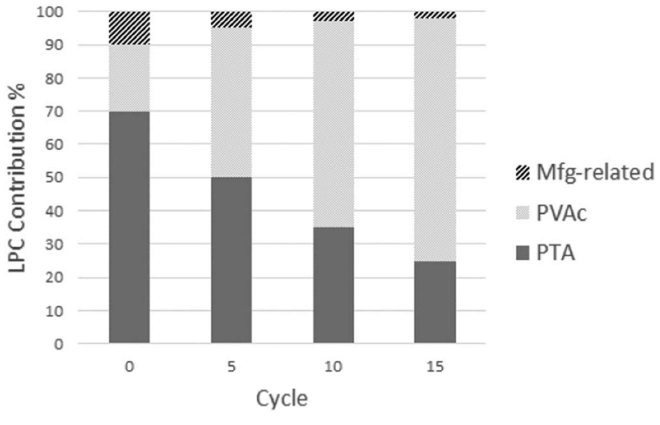

Figure 9. LPC contribution % by organic source over time (cycle no.).

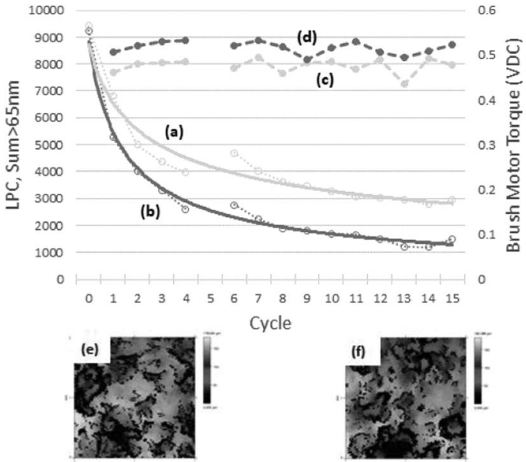

Figure 10. (a) DIW-only LPC decay, (b) 0.29% NH_4OH LPC decay, (c) DIW-only torque trend, (d) 0.29% NH_4OH torque trend, (e) DIW-only POST-nodule morphology Sa∼11.1µm, (f) 0.29% NH_4OH POST-nodule morphology Sa∼11.8µm.

Conclusions

The entire PVAc ecosystem is critical for brush quality, performance, and more specifically, break-in behavior. There are many factors that influence the break-in performance of the PVAc brush, many which are out of the brush manufacturers' control. Environmental effects, transportation and storage, brush handling, and post-CMP

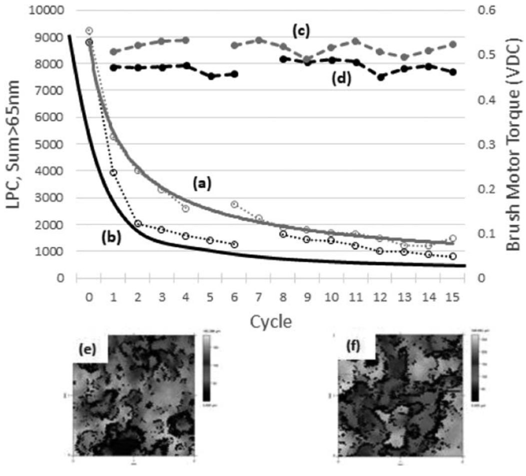

Figure 11. (a) Standard NH_4OH break-in LPC decay, (b) Optimized NH_4OH break-in LPC decay, (c) Standard NH_4OH torque trend, (d) Optimized NH_4OH torque trend, (e) Standard NH_4OH break-in POST-nodule morphology Sa∼11.8µm, (f) Optimized NH_4OH break-in POST-nodule morphology Sa∼17.1µm.

clean chemistry acclimation are significant factors investigated in this study. While development effort continues to reduce PVAc brush manufacturing-related releasable contamination, environmental effects are largely unavoidable and post-CMP chemistry acclimation can take many forms. Given the range of proprietary post-CMP chemistries used for sub-7nm logic and VNAND memory technologies, PVAc acclimation effects may include additional acid or base hydrolysis of residual byproducts, metal chelation or precipitation effects, oxidation-degradation, and/or lubrication (frictional) effects which alter brush surface properties. PVAc brushes should be managed and handled carefully inside and outside the fab; however, offline PVAc brush break-in may be the most economical way to recover lost CMP tool utilization and efficiently break-in the PVAc brush, perhaps with lower chemistry consumption. Mechanical forces and brush dynamics resemble actual post-CMP conditions but can be optimized (e.g. made more aggressive) without risking damage to costly production post-CMP cleaners.

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