Proceedings of 6th International Conference on Materials Chemistry and Environmental Engineering
DOI: 10.54254/2755-2721/2026.31957

One-Pot Synthesis of CeO_2-SiO_2 Composite Abrasives for High-Performance Chemical Mechanical Planarization: Synergistic Chemical-Mechanical Polishing

Junjie Xue[1], Haining Zhang[1], Shuming Wu[1], Bo Gao[1], Fangwei Lu[1], Chengrui Xin[1], Yan Zhao[2], Simin Li[1*], Hui Shen[1]

[1]The College of Energy Materials and Chemistry, Inner Mongolia University, Hohhot, China
[2]BaoTou TianJiao Seimi Rare Earth Polishing Powder Co., Ltd, Baotou, China
**Corresponding Author. Email: siminli@imu.edu.cn*

Abstract. CeO_2-SiO_2 hybrid abrasives are fabricated in one shot without any fancy multistep nonsense, and by tweaking the Ce:Si ratio to 1:3 ($CeSi_3$), removal rates climb while surfaces get smoother, especially when you throw in some 4-morpholinoethylsulfonic acid that prevents the CeO_2 suspension from clumping like bad coffee grounds, as AFM images confirm scratches vanish post-polish since $CeSi_3$'s chemical handshake spreads stress evenly during lapping and outperforms lazy physical blends by miles, making this not just lab chatter but a legit blueprint for next-gen CMP slurries.

Keywords: chemical mechanical polishing, CeO_2, surface modification

1. Introduction

Chemical mechanical planarization (CMP)—leveraging synergistic chemical etching and mechanical abrasion—has become indispensable for attaining nanometer-level global planarity in advanced IC manufacturing [1,2], while the demands of modern fabs such as sub-angstrom surface purity, blistering removal rates, and die-to-die uniformity expose severe limitations in legacy polishing schemes [3] because at the core lie slurry-borne particulates whose colloidal stability and interfacial reactivity dictate CMP performance outright, Industry today relies chiefly on three abrasive lineages: silica-derived (SiO_2), ceria-centric (CeO_2), and alumina-based (Al_2O_3), and particularly in chipmaking, CeO_2 abrasives command growing favor not merely for their redox-driven surface passivation traits (Ce^{3+}/Ce^{4+} shuttle dynamics) [4]. But also unmatched smoothing finesse, yet these particles carry fatal flaws as rampant agglomeration wrecks post-polish topography [5], Although SiO_2 colloids have excellent stability, their material removal rate is very low.

To tackle the clashing tech specs flagged earlier, we pitch CeO_2–SiO_2 composite bits as a fresh workaround since earlier work hints that slapping together a core-shell setup—SiO_2 stuck in the middle, CeO_2 wrapped tight around it—might crank up surface gloss while keeping removal rates punchy and flaws scarce, but old-school ways to build these combos, like drip-by-drip precipitation, gel-to-sol flips, or layer-by-layer self-stacking tricks, usually mean grinding through fussy steps and patchy shell wraps, and these nagging hiccups slam the brakes on whipping up next-level slurries needed to carve tomorrow's microchip guts.

Subsequent surface modification with 4-morpholinoethylsulfonic acid (MES) not only enhanced the suspension stability of the composite abrasive through electrostatic stabilization and steric hindrance effects but also significantly reduced surface defects caused by particle adhesion. This research provides a straightforward and scalable preparation pathway for advanced chemical mechanical polishing slurries. While meeting the critical requirements of semiconductor manufacturing below 10 nanometers, it also establishes a theoretical foundation for formulating abrasive design principles.

2. Experimental

2.1. Materials

Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.5%), aqueous ammonia solution ($NH_3 \cdot H_2O$, 30%), 4-morpholineethanesulfonic acid ($C_6H_{15}NO_5S$, 99%), tetraethyl orthosilicate (TEOS, $(C_2H_5O)_4Si$, 99%), and absolute ethanol (CH_3CH_2OH, 99.7%) were supplied by Innochem Technology Co., Ltd. (Beijing, China). All reagents were used as received without additional purification. Deionized water was employed in all experimental procedures.

2.2. Synthetic procedures

The abrasives were prepared using the co-precipitation method. Anhydrous ethanol was added to a beaker, followed by the addition of 0.05 mol cerium nitrate and 0.05 mol tetraethyl orthosilicate. The mixture was stirred until complete dissolution of cerium nitrate, followed by 30 minutes of ultrasonication to ensure homogeneous mixing. Ammonia water was then added dropwise to the mixed solution at a rate of 7.5 mL/min using a peristaltic pump until excess was achieved. After completion of the reaction, the solution was aged for 12 hours. The product was then centrifuged and vacuum-dried at 80 °C in a vacuum oven. Subsequently, the sample was transferred to a muffle furnace and calcined at 600 °C for 12 hours. The resulting sample was designated as CeSi (Figure 1). When the silicon source was proportionally scaled up, the prepared samples were named $CeSi_2$, $CeSi_3$, and $CeSi_4$, respectively. Samples prepared without the silicon source were designated as CeO_2, while those prepared without the cerium source were named SiO_2.

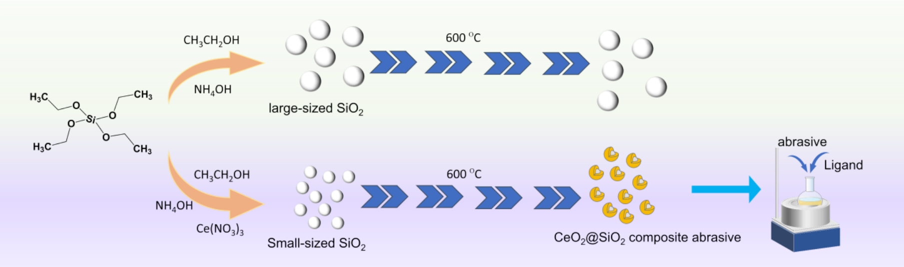

Figure 1. Schematic diagram of the synthesis mechanism for composite abrasives

2.3. Chemical mechanical polishing

Polishing performance tests were conducted using the POLI-400L CMP polishing machinet (G&P Technology, Inc.) at room temperature with a polyurethane Gas_Pad_16in_GP pad. The specifications of the silica wafer are as follows: 4-inch single-side polished, double-side oxidized, Ptype (100) orientation, thickness 525 ± 25 μm, oxide layer thickness 1000 nm, resistivity 1–5 Ω cm (purchased from KaihuaJingmei Silicon Material Company). The CMP process was conducted using a slurry concentration of 0.2 wt% with a polishing duration of 60 seconds. The platen and head speeds were set to 87 rpm and 93 rpm, respectively, while the polishing slurry was supplied at a rate of 300 mL/min. The applied pressure during polishing included a wafer pressure of 290 g/cm² and an R-ring pressure of 300 g/cm².

3. Results and discussion

Figure 2(a) schematically illustrates the one-pot synthesis process of ceria-silica composite abrasives. The typical preparation procedure was as follows: cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and tetraethyl orthosilicate (TEOS) were uniformly dispersed in ethanol under vigorous stirring, followed by dropwise addition of ammonia solution ($NH_3{\cdot}H_2O$) at 7.5 mL/min using a peristaltic pump to initiate simultaneous hydrolysis-condensation reactions. Under alkaline conditions, TEOS hydrolysis gradually formed silica nuclei while the cerium precursor hydrolyzed to form $Ce(OH)_3$ intermediates. After aging for 12 hours, the colloidal suspension was centrifuged and washed to remove unreacted ions and byproducts, vacuum-dried at 80°C, and the mixture was subsequently sintered in a muffle furnace to yield a CeO_2-SiO_2 composite abrasive with an adjustable ratio. To systematically investigate the composition-structure-property relationships, six samples were prepared by adjusting the Ce:Si precursor molar ratios: pure CeO_2 (b), Ce:Si=1:1 (c), 1:2 (d), 1:3 (e), 1:4 (f), and pure SiO_2 (g).

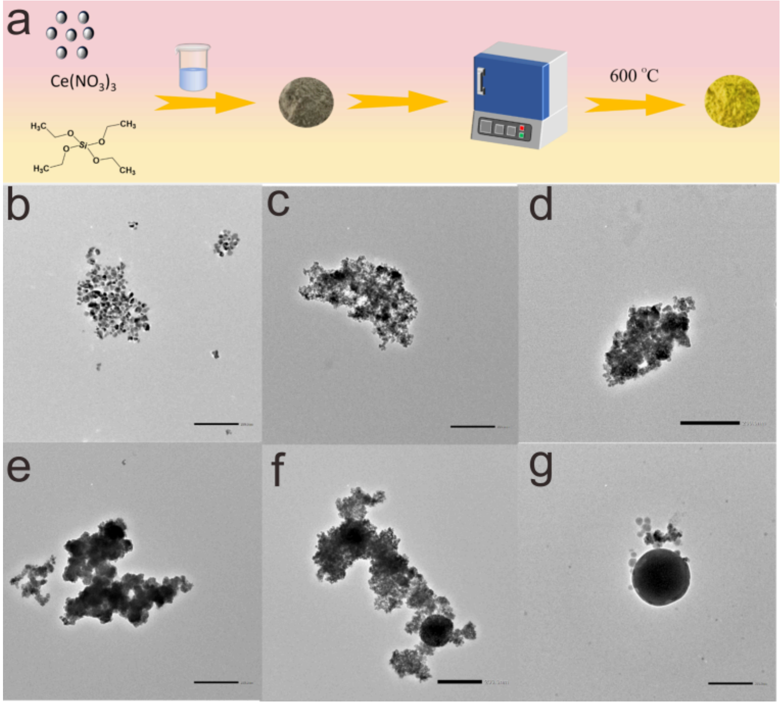

Figure 2. Schematic diagram of the one-pot synthesis process for composite abrasives (a). TEM images of CeO_2 (b), CeSi (c), $CeSi_2$ (d), $CeSi_3$ (e), $CeSi_4$ (f) and SiO_2 (g)

Cerium oxide's material removal power stems from Ce^{3+} sites on its surface engaging the substrate—a so-called "chemical bite," and since more Ce^{3+} usually means faster polishing, we checked this via XPS to map surface chemistry of composite particles, where survey scans showed that as silicon precursor rose, Si and O atomic shares climbed with Si 2p signal growing while binding energy shifted upward (Fig. 3a), Ce 3d deconvolution (Fig. 3c) pinned Ce^{4+} peaks at 916.8 eV (U_3), 907.4 eV (U_2), 900.9 eV (U) in $3d_{3/2}$ while Ce^{3+} sat at 903.4 eV (U_1), and in $3d_{5/2}$, Ce^{4+} signals hit 898.3 eV (V_3), 888.9 eV (V_2), 882.4 eV (V) whereas Ce^{3+} marked 884.9 eV (V_1), with surface Ce^{3+} fraction climbing as U_1/V_1 area ratio widens, O 1s profile (Fig. 3d) revealed oxygen defect shifts by resolving three O types: lattice O^{2-} at 529.3 eV, vacancy-bound O at 532.1 eV, and physisorbed O at 533.7 eV, where the last one's intensity kept rising.

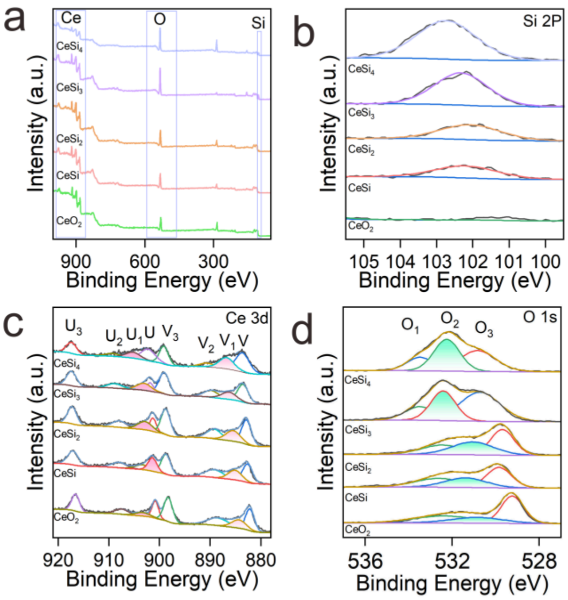

Figure 3. XPS full spectrum (a), Si spectrum (b), Ce spectrum (c) and O spectrum (d)

Under standard CMP conditions (full specs in Table 1), the CeSi3 composite—with its cerium:silicon molar ratio fixed at 1:3—delivered maximum material removal rate (see Fig. 4) because CeO_2's catalytic surface behavior doesn't just coexist with SiO_2's mechanical grit but actively collaborates, as nano-CeO_2 patches latch onto the wafer's native oxide through redox-triggered bonding when polishing kicks off, spawning an interfacial cerium silicate layer that mechanically undermines substrate cohesion while the stiff silica skeleton swoops in to exploit that weakness via shear-driven flaking and boost excision throughput, Higher silicon loading (maxed at CeSi3) cranked up removal speed, fitting snugly into the dual-mechanism model since more Si means harder abrasion yet enough CeO_2 sites remain to keep chemically softening the surface, although oddly CeSi4 (1:4 ratio) underperformed even with extra silicon onboard due to twin bottlenecks where holding slurry concentration steady at 0.2 wt% leaves CeO_2 scarcity unable to replenish reactive zones fast enough for continuous weakening while silicon overload shifts the game toward raw grinding which proves inefficient for oxide films, Pure CeO_2's lousy showing further proves particle size and colloid stability call the shots in CMP, as ultrafine CeO_2 (Fig. 5a) packs more reactivity thanks to sky-high surface-to-volume ratios but without sufficient downforce its cutting edge fizzles, making it clear that top-tier planarization needs engineered composites where chemical activation and structural heft don't just coexist but choreograph.

Table 1. Contents of Ce^{3+} and oxygen vacancies in CeO_2, CeSi, $CeSi_2$, $CeSi_3$ and $CeSi_4$ abrasives

Samples	Ce^{3+}	Oxygen vacancy
CeO_2	20.58	35.41
CeSi	19.33	33.64
$CeSi_2$	24.19	36.72
$CeSi_3$	31.23	46.50
$CeSi_4$	33.17	47.62

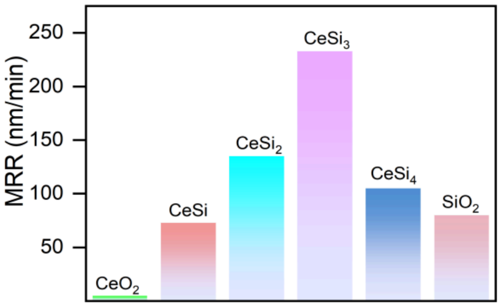

Figure 4. MRR of CeO_2, CeSi, $CeSi_2$, $CeSi_3$, $CeSi_4$, and SiO_2

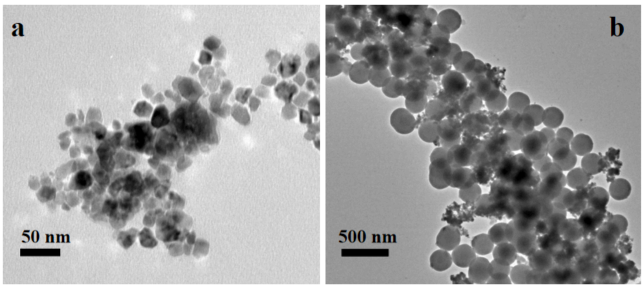

Figure 5. TEM image of CeO_2 (a) and SiO_2 (b)

Unlike plain SiO_2 spheres, the hybrid abrasive shows stark structural shifts (Fig. 5b), and when made under identical conditions—minus any cerium salt—the average size of pure silica bits hits ~200 nm, yet inside the composite, the silica cores visibly shrink down to 100–150 nm range because Ce^{3+} messes with early silica nucleation kinetics, as during co-synthesis, trivalent cerium acts like Lewis acid hotspots by cranking up TEOS breakdown through yanking electrons from Si–O–C_2H_5 bonds, which according to classic nucleation theory means more nuclei equal more tiny silica embryos, and these nano-cores trapped in the matrix deliver a double win for CMP since higher surface/volume ratios mean better ceria docking spots while their small scale lets pressure spread gentler during polishing to slash micro-scratch odds, and synergy between outer CeO_2 skin and mini silica hearts supercharges chemomechanical bite not just from curvature-strained ceria shells boosting oxygen vacancies but also by forcing more CeO_2-wafer collisions that keep Ce–O–Si bridges multiplying like rabbits.

Suspension stability is a key indicator for evaluating the performance of polishing slurries. Although mixed abrasives generally combine with colloids more easily than single-phase abrasives, they still fall short under the extreme requirements of high-end slurries. To address this, we grafted organic ligands onto composite particles using a chaotic yet effective method: 5 grams of abrasive was added to 250 milliliters of water, approximately 0.2 grams of MES was added without precise measurement, and the mixture was heated in an oil bath at 100°C for 12 hours, followed by centrifugation, drying, and polishing tests. Although the material removal rate slightly decreased, surface smoothness significantly improved, and slurry stability was markedly enhanced. The sample with the highest polishing rate, CeSi3 (labeled as m@CeSi3 after modification), was selected for further characterization. XRD in Figure 6a shows that its diffraction peaks perfectly match the reference angles of CeO_2, while the amorphous signal of SiO_2 causes almost no interference; FTIR in Figure 6b exhibits a distinct band at 830 cm^{-1}, corresponding to the MES carbon skeleton feature reported in the literature, and Figure 7 details the remaining characteristic peaks of CeO_2 and SiO_2; BET data in Figure 6c indicates a reduction in nitrogen adsorption, possibly due to steric hindrance or particle dispersion caused by the ligands; XPS spectra in Figures 6d-f (including survey, Ce 3d, and O 1s) show negligible changes in composition. It is ultimately confirmed that the decrease in polishing rate is due to the ligands partially shielding the direct contact between the abrasive surface and the substrate, thereby reducing the strength of single-cycle mechanical engagement.

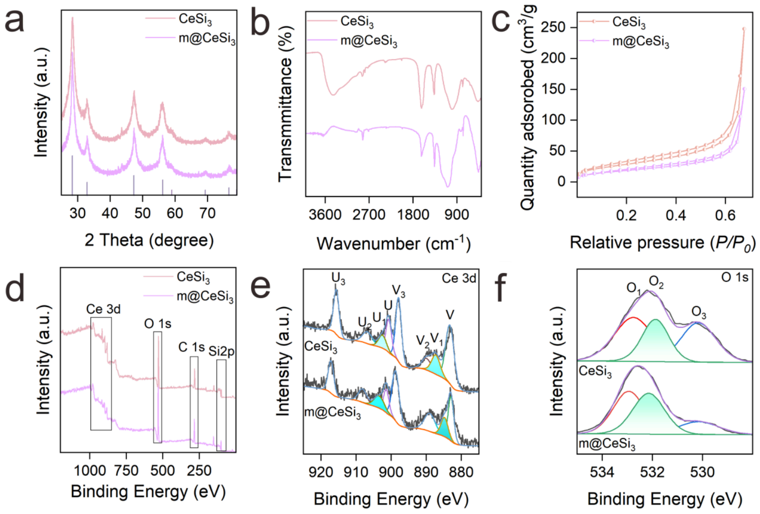

Figure 6. XRD patterns before and after modification (a), FTIR spectra (b), N_2 absorption/desorption isotherms (c), XPS Full Spectrum (d), Ce spectrum (e) and O spectrum (f)

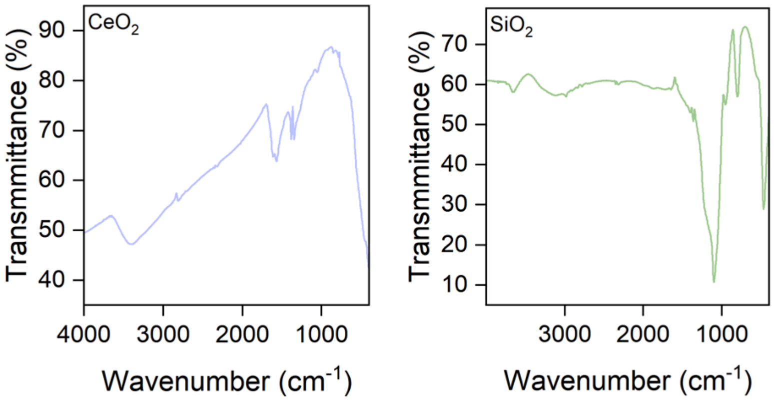

Figure 7. FTIR spectra of CeO_2 and SiO_2

To systematically evaluate the polishing performance of synthetic abrasives and their interfacial interaction mechanisms, this study employed atomic force microscopy to analyze the surface topography and defect distribution of polished substrates. We compared three distinct abrasive systems: mechanically blended SiO_2-CeO_2 composite abrasive (mass ratio 3:1), one-pot synthesized $CeSi_3$ hybrid abrasive, and surface-modified m@$CeSi_3$ abrasive. This comparative analysis clearly reveals the key advantages of the one-pot synthesis strategy and the structural optimization effects achieved through surface modification. Figure 8a displays AFM analysis results for the mechanically mixed SiO_2-CeO_2 system. Despite theoretical optimization of the abrasive ratio, the polished surface exhibited pronounced defects. This indicates poor interface compatibility between the two oxide phases, preventing effective synergistic material removal mechanisms. The mechanical mixing process failed to establish chemical bridging between components, leading to abrasive agglomeration and localized stress concentration during polishing. In contrast, the $CeSi_3$ hybridized abrasive (Figure 8b) exhibits markedly improved surface quality. The chemical hybridization process promotes uniform distribution of polishing stresses through dual synergistic effects, consistent with prior research findings. The further optimized m@$CeSi_3$ system (Figure 8c) achieves superior surface integrity, demonstrating enhanced overall performance.

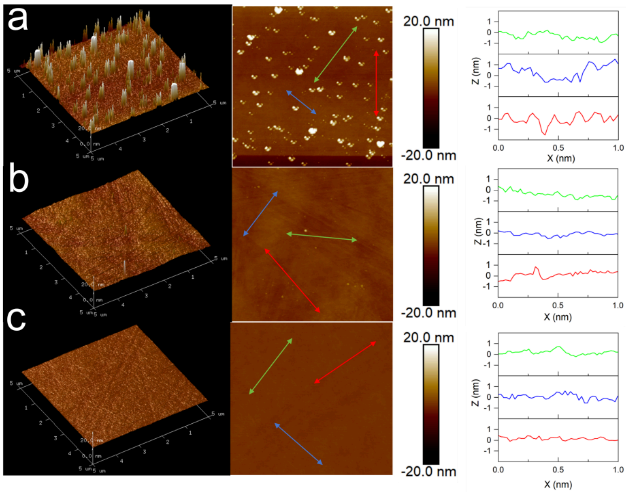

Figure 8. AFM of mechanically mixed SiO_2-CeO_2 composite abrasives (a). AFM of $CeSi_3$ hybrid abrasives (b) and AFM ofm@$CeSi_3$ hybrid abrasives (c)

4. Conclusion

This study successfully synthesized CeO_2-coated SiO_2 composite abrasives via a one-pot strategy. By precisely controlling the cerium-silicon precursor ratio and reaction kinetics, we achieved CeO_2 deposition onto monodisperse SiO_2 cores. Among these, the sample with a Ce:Si molar ratio of 1:3 ($CeSi_3$) exhibited the most favorable comprehensive properties. Characterization revealed that the $CeSi_3$ abrasive achieves low surface roughness while maintaining high material removal rates, outperforming both CeO_2 and SiO_2 monocomponent abrasives. This enhanced polishing efficiency stems from the synergistic interaction between the chemical reactivity of CeO_2 and the mechanical strength of SiO_2: during chemical mechanical planarization, CeO_2 nanoparticles chemically soften the wafer surface via Ce^{3+}/Ce^{4+} redox reactions, forming a weakened Ce-O-Si interface layer. Concurrently, the harder SiO_2 core removes this softened layer through mechanical shearing action. XPS further validated this dual-action mechanism, with data indicating significantly increased Ce^{3+} content and oxygen vacancy concentration on the composite abrasive surface. Surface modification using MES improved both the suspension stability of the abrasive and the planarity of the polished surface. Atomic force microscopy analysis demonstrated that the chemically hybridized $CeSi_3$

abrasive outperformed the mechanically mixed SiO_2–CeO_2 system in polishing efficacy. The one-pot synthesis strategy ensures uniform stress distribution and effectively suppresses abrasive agglomeration, which is crucial for achieving low-defect surfaces.

Acknowledgements

H. Shen acknowledges the financial support from the National Key R&D Program of China (2023YFB3507100). S. Li acknowledges the financial support from the Natural Science Foundation of Inner Mongolia (2025QN02068) and Start-Up Funding of Inner Mongolia University (10000-A24202027).

References

[1] Lee, H.; Kim, H.; Jeong, H. Approaches to sustainability in chemical mechanical polishing (CMP): a review. Int. J. precis. eng. manuf-green. technol. 2022, 9, 349-367.
[2] Michalowska-Forsyth, A. More than scaling: CMOS-integrated circuits in the third decade of the 21st century. Elektrotech. Inftech. 2024, 141, 1-2.
[3] Alety, S. R.; V. Sagi, K.; Babu, S. V. Role of Ce^{3+} Ions in Achieving High Silicon Nitride Polish Rates. ECS J. Solid State Sci. Technol. 2017, 6, P898.
[4] Zhao, X. Y.; Han, X. Y.; Tan, B. M.; Zhao, J. D.; Qi, W. Y.; Geng, J. J.; Shi, Y. H.; Huang, Y. Y. Research progress of ceria abrasives in STI CMP: optimization and application. Int. J. adv. manuf. technol. 2025, 140, 4625-4642.
[5] Wang, Y.; Zhang, B. G.; Wu, P. F.; Liu, M.; Cui, D. X.; Xian, W. H. Improving the dispersion stability and chemical mechanical polishing performance of CeO_2 slurries. ECS J. Solid State Sci. Technol. 2023, 12, 044004.