Non-spherical abrasives with ordered mesoporous structures for chemical mechanical polishing

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ABSTRACT The chemical mechanical polishing (CMP) technology has been widely used for surface modification of critical materials and components with high quality and efficiency. In a typical CMP process, the mechanical properties of abrasives play a vital role in obtaining the ultra-precision and damage-free surface of wafers for improvement of their performances. In this work, a series of fine structured rod-shaped silica (RmSiO₂)-based abrasives with controllable sizes and diverse ordered mesoporous structures were synthesized *via* a soft template approach, and successfully applied in the sustainable polishing slurry for improving the surface quality of cadmium zinc telluride (CZT) wafers. Compared with commercial silica gel, solid and mesoporous silica spheres, the RmSiO₂ abrasives present superior elastic deformation capacity and surface precision machinability on account of their mesoporous structures and rod shapes. Especially, ultra-precision surface roughness and relatively effective material removal speed were achieved by the CMP process using the RmSiO₂ abrasives with a length/diameter (L/d) ratio of 1. In addition, a potential CMP mechanism of the developed polishing slurry to CZT wafer was elucidated by analyzing X-ray photoelectron spectra and other characterizations. The proposed interfacial chemical and mechanical effects will provide a new strategy for improving abrasives' machinability and precision manufacture of hard-to-machine materials.

Keywords: non-spherical abrasives, mesoporous structure, chemical mechanical polishing, interfacial mechanochemistry

INTRODUCTION

It is vital to achieve a globally planarizing surface of key

materials and components with high quality and efficiency, which has a significant impact on the performances of devices in the major fields of aeronautics and astronautics, new energy devices, and so on [1–5]. Up to now, chemical mechanical polishing (CMP) technology is one of the most efficient approaches to obtain ultra-smooth and damage-free surfaces globally or locally by synergistically coupling the dual effects of mechanical grinding and chemical etching [6–9]. Moreover, the CMP conditions and slurry compositions directly determine the surface topography of polished wafers. However, the polishing effect of optimizing experimental parameters in the CMP process is limited [10–13]. Therefore, the development of a novel polishing slurry is desirable for improving the accuracy and efficiency of CMP [14–19]. As one of these components, abrasives are critical for removing the corrosion layer by mechanical grinding in a typical CMP process. Thus, the properties of abrasives play a vital role in the CMP performance [20–24].

So far, great efforts have been devoted to modifying the morphology [25–29], structure [30–37], and even surface chemical state of abrasives [38–41]. It is worth noting that the porous abrasives present potential applications in bringing the surface accuracy to an atomic level because of their low elasticity modulus (E) [42–45]. For example, as previously reported, porous silica abrasives turn out to be a better choice than conventional solid spheres due to their superior surface-flattening and damage-eliminating abilities, which can be attributed to their preferable elastic deformation ability [43,46,47]. In fact, the dependence of E values on porous silica shell thicknesses in the core-

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mesoporous shell structured composites has been largely vindicated in some literatures [48–50]. Moreover, Jauffrès *et al.* [51] concluded employing nanoindentation and finite element model that mesoporous thin silica films with a lattice-ordered porosity exhibit a higher indentation modulus and a more elastic recovery behavior relative to random macroporous ones. In addition, the molecular dynamics (MD) simulation results also demonstrated that the friction force in nanoscale is linearly correlated to the quantity of chemically interacting atoms across the contact, which means the porous abrasives maybe possess well-defined tribo-chemical property due to their high specific surface area [52]. With further study, it is increasingly recognized that the porous abrasives have lower E than non-porous ones due to their spring-like structure, which can promote their mechanical property and be beneficial to surface planarization.

However, most of the reports focused on the improvement of CMP quality by porous spherical abrasives, rather than the mechanism of porous structure affecting their elastic deformation properties and polishing effect. Therefore, the influence of the pore structure of porous abrasives on their mechanical properties is inexplicit, which would undoubtedly restrain the research on the improvement of abrasive properties. Furthermore, it is well-known that CMP quality and efficiency are restricted mutually, and thus the improvement of polishing efficiency by porous abrasives is restricted even though it is beneficial for enhancing the precision of CMP process.

However, there is no report to modify abrasives in multiple properties (e.g., the porous structure and morphology) to improve their polishing quality and efficiency simultaneously.

Herein, a series of rod-shaped mesoporous silica particles (RmSiO_2) with diverse length to diameter (L/d) ratios were designed to investigate the effects of both mesoporous structure and rod shape on the tribo-chemical ability of abrasives. Moreover, a kind of sustainable polishing slurry was developed based on these particles. Cadmium zinc telluride (CZT) is a crucial third-generation semiconductor material for high-energy detectors at room temperature. However, owing to its soft and brittle texture, CZT wafers are regarded as a hard-to-machine material [53–56]. Therefore, the prepared slurry was applied in the CMP process of CZT wafers to make a thorough inquiry into the CMP performance of this series of RmSiO_2 abrasives. The schematic illustration of the overall experimental design for the synthesis of RmSiO_2 abrasives and the CMP process is shown in Fig. 1. Furthermore, the dependency of porous structure and mechanical properties of RmSiO_2 particles on different L/d ratios was investigated by measuring the E values *via* the atom force microscopy (AFM) non-indentation technique. In addition, the possible CMP mechanism of the developed polishing slurry containing RmSiO_2 abrasives to CZT wafers was proposed, which might provide further insights to disclose the CMP mechanism of other materials.

Figure 1 Schematic illustration of the overall experimental design for the synthesis of RmSiO_2 abrasives and the CMP process.

EXPERIMENTAL SECTION

Chemicals

Absolute ethanol (EtOH, 99.7%), ammonia solution ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25.0%–28.0%), hexadecyltrimethylammonium bromide (CTAB, 99.0%), tetraethyl orthosilicate (TEOS, 28.4%), and tannic acid (TA) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrogen peroxide (H_2O_2 , 30%) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The commercial silica sol (SiO_2 , 60 wt%) with an average diameter of 60 nm for contrast experiment was purchased from Dalian Snowchemical Co., Ltd., whose transmission electron microscopy (TEM) image is shown in Fig. S1a. All reagents in the experiments were of analytical grade and used directly without any further purification. Deionized water (DI H_2O) was used throughout all experiments.

Synthesis of RmSiO_2 abrasives

RmSiO_2 particles were prepared *via* a modified Stöber method. The molar ratios of reactants for synthesizing RmSiO_2 particles with different L/d ratios are listed in Table S1. The synthesis process is as follows: primarily, certain amounts of DI H_2O , EtOH and $\text{NH}_3\cdot\text{H}_2\text{O}$ solution were mixed at room temperature under a stirring speed at 200 r min^{-1} . Then CTAB as a structure-directing agent was dissolved into the mixture and treated in an ultrasonic bath for 15 min to form a self-assembly template solution. Subsequently, TEOS as a silica source agent mixed with EtOH was added dropwise into the template solution above under continuous stirring within 23–55 min. A homogeneous milky colloidal solution was gradually formed after reaction for 4 h. Ultimately, the as-prepared RmSiO_2 particles were collected by centrifugation, washed with DI H_2O and EtOH several times and dried overnight at 60°C . Finally, RmSiO_2 particles with different L/d ratios were synthesized successfully after soft template removal by calcining at 550°C for 4 h in air. For comparing the mechanical properties of the as-synthesized mesoporous RmSiO_2 , solid and mesoporous silica spheres (sSiO_2 and mSiO_2) abrasives, sSiO_2 and mSiO_2 spheres with a uniform particle size of 422 and 391 nm were prepared through a typical Stöber synthesis (see Supplementary information for experimental details), respectively. The TEM images are shown in Figs S1b and S2a.

CMP tests

CZT wafers with $1.0\text{ cm} \times 1.0\text{ cm}$ in dimension and 1.3–1.4 mm in thickness, grown by the modified Bridg-

man method were used as polishing substrates. In the experiments, three pieces of CZT wafers were glued by using molten paraffin wax along the periphery of an aluminum disk with 100 mm diameter evenly. The lapping and CMP experiments were performed on a precise polishing equipment (UNIPOL-1200S, Shenyang Kejing auto-instrument Co., Ltd., China) with a corrosion-resistant plate. Before the CMP experiment, the CZT wafers should be ground with 4000-grit SiC paper first to obtain a relatively flat surface. During grinding, the load pressure was 30 kPa, and the rotation speed of SiC paper was 50 r min^{-1} . DI H_2O was used as a grinding fluid and supplied at a flow rate of 10 mL min^{-1} . After 1 min grinding, the CZT pieces were rinsed with DI H_2O and blow-dried with compressed air for further precise polishing.

The commercial SiO_2 , mSiO_2 , sSiO_2 , and RmSiO_2 abrasives with different L/d ratios were used to prepare CMP slurries with a concentration of 45.5 g L^{-1} in aqueous suspensions. In addition, H_2O_2 solution, polyethylene glycol ($M_w = 2000$, PEG2000), and TA were applied as oxidant, dispersant and pH adjuster, respectively. The volume ratio between aqueous suspensions and H_2O_2 solution was 6.5, and 5 wt% PEG2000 was added in slurries based on the weight of abrasives. The pH value of CMP slurries ranging from 3.95 to 4.05 was adjusted by adding 1 mol L^{-1} TA dropwise. Subsequently, the CMP slurries were treated ultrasonically for 30 min before CMP experiments. During the CMP experiment, the SiC paper should be replaced by a black porous neoprene pad (MD-chem, NX-MT), and the parameters of the CMP process were set as per Table S2. After CMP, the CZT pieces were taken down by molten paraffin wax and cleaned with EtOH at 80°C in an ultrasonic bath, followed by wiping clean with a dust-free cloth.

Characterization

The morphologies of the RmSiO_2 particles were characterized by TEM (HITACHI HT7700) at an acceleration voltage of 100 kV and scanning electron microscopy (SEM, FEI Quanta 200F) operating at 20 kV. High-resolution SEM (HRSEM, HITACHI S5500) were carried out to track the mesopore distribution on the RmSiO_2 particle surface. The samples for TEM, SEM and HRSEM were prepared by dispersing them into EtOH under ultrasonic treatment and dropping the mixture onto a commercial carbon film-coated copper grid and conductive glue, respectively. The size distribution of the RmSiO_2 particles was obtained by counting 80 nanoparticles from SEM images at random and recording their

length and diameter values. Nitrogen (N_2) adsorption/desorption isotherms were performed with a Micromeritics ASAP 2469 apparatus to detect the surface areas and pore volumes of the $RmSiO_2$ particles, based on the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The powder X-ray diffraction (XRD) patterns and corresponding low-angle XRD patterns were undertaken on a Rigaku D/Max2500PC diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over the 2θ range of 5° – 80° and 0.5° – 8° , respectively. Besides, the scanning speed at room temperature was 5° min^{-1} and 1° min^{-1} , respectively. The E measurements were conducted by AFM (Bruker) with the contact mode, and the antimony-doped Si probe with a spring contact of 72.488 N m^{-1} was used to compress the particle to deform for 12 nm.

The topography of CZT wafer surface before and after CMP experiments with different abrasives was imaged by an optical microscope (MX-40, Olympus, Japan) and AFM (Multimode Nanoscope V) using a commercial silicon probe. The cantilever had a pyramid-shaped tip with a curvature of the apex around 20 nm. The scan areas with a resolution of $250 \text{ px} \times 250 \text{ px}$ were set as $5 \text{ \mu m} \times 5 \text{ \mu m}$ and scan speeds were 1 Hz. For objectively evaluating the polishing accuracy, the average mean roughness (Ra_{average}) and root-mean-square (RMS) roughness (Rq_{average}) values of surfaces of polished CZT wafers were acquired by measuring randomly five selected locations and calculating their average values. The two-dimensional (2D) and 3D images shown are the height maps of CZT wafers with the lowest Ra values among the five selected locations. The material removal rate (MRR, nm h^{-1}) could be calculated as Equation (1):

$$\text{MRR} = \frac{\Delta m \times 10^6}{\rho S \tau}, \quad (1)$$

where Δm is the mass loss of CZT wafers after polishing (g); ρ is the density of CZT wafers ($\rho_{\text{CZT}} = 5.925 \text{ g cm}^{-3}$); S is the total contact area between the polishing pad and CZT substrates (mm^2); τ is the polishing time (h).

The Tafel polarization curves were recorded by an advanced electrochemical system (CHI 760E, Chinstruments Co., Ltd.) with a three-electrode system. The referenced and auxiliary electrodes were saturated calomel electrode (SCE) of potassium chloride (KCl) and platinum (Pt) with a purity of 99.99%, respectively. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra^{DLD} KRATOS spectrometer using a monochromated Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$). All binding energies were referenced to the C 1s peak (284.6 eV). Fourier-transform infrared

(FTIR) spectroscopy measurements were performed on a Nicolet 6700 spectrometer to detect the vibrational peaks of TA and catechol- $\text{Cd}^{2+}/\text{Zn}^{2+}$ mono-complexes. In order to obtain the complexes, the CZT substrates were ground into a powder, and immersed in a solution composed of DI H_2O , H_2O_2 and TA with pH of 4 for 4 h. Finally, the solution was dried in a vacuum oven at 60°C to obtain a kind of brown powder as the chelating product.

RESULTS AND DISCUSSION

Structural characterizations of $RmSiO_2$

$RmSiO_2$ particles with different L/d ratios of 1, 1.5, 2, 2.5 and 3 ($RmSiO_2$ -1, $RmSiO_2$ -1.5, $RmSiO_2$ -2, $RmSiO_2$ -2.5 and $RmSiO_2$ -3, respectively) were prepared *via* a modified Stöber method. Their morphologies and structural characterizations *via* SEM and TEM are shown in Fig. 2. The uniform rod-shaped structures can be seen clearly from SEM images in the first column of Fig. 2 with a regular and homogeneous shape, and the $RmSiO_2$ particles are highly monodispersed with no aggregation between them. TEM images (Fig. 2) also indicate all the $RmSiO_2$ particles with different L/d ratios have similar rod-shaped structures like cylinders with removed edges. The average sizes of the $RmSiO_2$ particles were calculated through their narrow length and diameter distributions, which reveal the change in L/d ratios was mainly due to the increase in their length.

Due to the electron contrast possibly resulting from the existence of porous frameworks [57], it is observed that mesopores and channels distribute radially on the particles in TEM images. In order to detect the distribution of mesopores more clearly, the individual particles with L/d ratios of 1, 2, 3 were magnified. As confirmed by HRSEM images (Fig. 3), abundant mesopores scatter throughout the particles, causing their smooth outer surface to be relatively porous. However, it is worth noting that the distributions of pores are slightly diverse with the change of L/d ratios. The $RmSiO_2$ -1 particle possesses relatively dense pores, and most of them are arranged in parallel lines to form well-ordered hexagonal pore structures, as shown in Fig. 3d. However, the bigger the L/d ratios, the looser the pores. The degrees of pore structural order gradually decrease with increases in L/d ratios, until the well-ordered porous frameworks vanish on the surface of the $RmSiO_2$ -3 particle. This may be attributed to the quantitative template agent used. According to the Stöber method, limited CTAB plays a role as a structural director in the formation of $RmSiO_2$ particles. When the length of $RmSiO_2$ particles becomes longer, the pores constructed

Figure 2 SEM images (a, e, i, m, q), TEM images (b, f, j, n, r), particles length (c, g, k, o, s), and diameter (d, h, l, p, t) distributions of RmSiO_2 particles with different L/d ratios.

Figure 3 HRSEM images with different magnifications of RmSiO_2 -1 (a, d), RmSiO_2 -2 (b, e), and RmSiO_2 -3 (c, f).

by a fixed amount of CTAB become less compact, so that the pores density and degree of their structural order decrease as the L/d ratios of RmSiO_2 particles increase.

To further explore the porous nature of the RmSiO_2 particles, the powder XRD patterns were carried out. All the wide-angle XRD patterns (Fig. 4b) of the RmSiO_2

Figure 4 (a) Powder low-angle XRD patterns and (b) wide-angle XRD patterns of RmSiO₂ particles with different L/d ratios.

particles with different L/d ratios present only one broad diffraction peak located near 23° , revealing the formation of amorphous silicon in the as-synthesized samples [58]. However, their low-angle XRD patterns (Fig. 4a) exhibit entirely different characteristics. Obviously, three discernible diffraction peaks and one weak peak, corresponding to (100), (110), (200) and (210) planes, respectively, appear only in low-angle XRD patterns of RmSiO₂-1, which demonstrates the RmSiO₂-1 has classical well-ordered hexagonal pore structures [59,60]. However, with increasing L/d ratios, not only do the intensities of the first peaks matched with (100) plane in low-angle XRD patterns of RmSiO₂-2 and RmSiO₂-3 become weaker, but the positions of the peaks also shift to higher angles. The reason is that the order degrees of pore structure decrease and the pore distribution is more concentrated, respectively. On account of the weakening of intensities and position shift of peaks, the low-resolution peaks cannot be displayed in low-angle XRD patterns.

Furthermore, the values of $d_{(100)}$ and $a_{(100)}$, representing interplanar spacing and pore center distance, can be calculated using 2θ values of (100) planes in low-angle XRD patterns *via* Bragg's Law. The computed $a_{(100)}$ values of RmSiO₂-1, RmSiO₂-2 and RmSiO₂-3 are 4.04, 3.69, and 3.51, respectively, implying the pores are increasing centralized with the increase of L/d ratios, which can be confirmed by HRSEM observations (in Fig. 3e, f). This is completely contrary to the changing trend of pore density on the whole, as shown in Fig. 3, that the pores of RmSiO₂ particles become sparse gradually with their size enlarging. This unique mesostructure arrangement on the RmSiO₂ surface can be attributed to their porous frameworks constructed by CTAB micelles. As the micelle arrangement is susceptible to the reaction environment during the self-assembly process, the pore structures with different local and global permutations are formed when

the ratios of reactants are different. Therefore, pores of RmSiO₂-1 particle are relatively unconsolidated than RmSiO₂-2 and RmSiO₂-3 within the small concentratedly distributed range, even though it has compact pores with well-ordered hexagonal structures overall.

N₂ adsorption/desorption isotherms (Fig. S3) provide further insight into porosity information (e.g., pore size, surface area and pore volume) of the RmSiO₂ particles. According to IUPAC, the isotherms can be assigned to the type IV isotherms with H1 hysteresis loops, implying the presence of typical mesoporous structure [61]. Moreover, the corresponding pore size distribution curves (Fig. S3b) were estimated by the BJH model using data from adsorption branches. The average pore diameters of RmSiO₂ particles with different L/d ratios are between 2 and 2.5 nm, which is in agreement with the mesoporous frameworks indicated by HRSEM and powder XRD results. On the other hand, the peak of RmSiO₂-1 centered at 2.4 nm is relatively posterior and sharper than others, which means that the RmSiO₂-1 has more large-sized pores than RmSiO₂-2 and RmSiO₂-3. This could be attributed to channel collapse and pore expansion in RmSiO₂-1's dense pore structure during the calcination process of silicate condensation. It is difficult for pores of RmSiO₂-2 and RmSiO₂-3 to expand due to their sparse pore arrangements overall, but their pores with a short pore center distance can expand easily within the small compact range. Therefore, the number of large-sized pores on RmSiO₂-2 and RmSiO₂-3's surfaces is less and their average pore diameters are relatively smaller than that of RmSiO₂-1 particles. Besides, the calculated BET surface area and BJH cumulative pore volume of RmSiO₂-1 are 1105 m² g⁻¹ and 0.78 cm³ g⁻¹, respectively, while those of RmSiO₂-2 and RmSiO₂-3 slightly decrease. This confirms that a large number of large-sized pores exist in RmSiO₂-1 compared with RmSiO₂-2 and RmSiO₂-3.

As seen from the above figures (Figs 3, 4 and Fig. S3), the prepared RmSiO₂ particles with different L/d ratios have diverse mesoporous structures. Since the porous characteristics of abrasives have a great influence on their mechanical properties, the E values of RmSiO₂ and sSiO₂ particles were calculated *via* the Johnson-Kendall-Roberts (JKR) model in AFM nano-compression measurement, shown in Fig. S4. It can be found that the E value of the sSiO₂ sphere is 6.078 GPa and higher than that of RmSiO₂ particle (2–4 GPa), confirming the porous abrasives deform more elastically than non-porous ones in a squeezed state. Moreover, the E value of RmSiO₂ particles increases with the increase of L/d ratios. The RmSiO₂-1 particle

with abundant compact pores possesses the lowest E , implying its favorable deformation capacity and mechanical performance in the CMP process. By contrast, the RmSiO_2 -3 particle is relatively less elastic, and more importantly, its E value is close to that of the RmSiO_2 -2. This might be because RmSiO_2 -2 and RmSiO_2 -3 have similar unconsolidated porous frameworks with out-of-order pore arrangements. Due to the pores of RmSiO_2 -2 particles are arranged more closely and orderly than for the RmSiO_2 -3 ones, E values of RmSiO_2 -2 particles are slightly lower. The measured results of Young's modulus reveal that the pores' arrangements and order degrees of abrasives have an impact on their mechanical properties.

CMP performance and mechanical mechanism of RmSiO_2

It is commonly recognized that surface quality and material removal speed are two crucial evaluating indicators of CMP performance, which are determined by the characterizations of abrasives and CMP conditions. Under the identical experimental processes, the chemical and mechanical nature of RmSiO_2 particles has a decisive impact on polishing performance.

The surface quality of polished CZT wafers can be evaluated through their surface topographies, which were achieved by optical microscope and AFM. The optical images of CZT wafers after grinding and polishing are observed with a large area of $1.5\text{ mm} \times 2.0\text{ mm}$ in Fig. S5. As can be seen in Fig. S5b, an abundance of mechanical scratches and cracks are distributed deeply on CZT wafers after grinding for 1 min. Conversely, the polished surfaces using the commercial and as-synthesized abrasives are perfectly flat and smooth like mirrors, revealing apparent removal of micro-sized asperities and grooves. However, compared with the spotless surface of CZT wafers polished with sSiO_2 , mSiO_2 , and RmSiO_2 abrasives, a few residual stains and micro-scratches have remained on the surface polished with commercial abrasives. This may be caused by their wide distribution of particle sizes, so the tiny ones are so sticky that cannot be removed and then embedded in the surface to cause micro-scratches. Moreover, the small pits on the surface of CZT wafer polished with sSiO_2 abrasives have a more distinct appearance than that of CZT wafers polished with mSiO_2 and RmSiO_2 abrasives. This indicates sSiO_2 abrasives would leave deeper grinding trails than mSiO_2 and RmSiO_2 abrasives when they bear the same loads in the CMP process.

To further explore the surface features of CZT wafers after polishing with RmSiO_2 , mSiO_2 , and sSiO_2 particles, AFM images scanning over $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ regions and

cross-sectional profiles (Fig. 5) were tracked. For pixels in AFM 2D and 3D images, the lighter the pixels, the higher their height, so an area filled with approximate colors represents that the corresponding surface has superior surface flatness and accuracy. Comparing five AFM 2D images (Fig. 5a–e) of CZT wafers polished with SiO_2 , mSiO_2 , and RmSiO_2 abrasives, the most uniform color can be found in the image of polished CZT wafer using RmSiO_2 -1, while the worst is the wafer using sSiO_2 . Moreover, the sequence of Ra values calculated using their height data are 0.259, 0.333, 0.339, 0.376, and 0.412 nm, matching to the surface accuracies of CZT wafers polished with RmSiO_2 -1, RmSiO_2 -3, RmSiO_2 -2, mSiO_2 , and sSiO_2 (CZT_{R1} , CZT_{R3} , CZT_{R2} , CZT_{m} , and CZT_{s} wafers), respectively. In addition, it is worth mentioning that the variation trend of Ra_{average} values and Rq_{average} values in Fig. 5f reflects the same sequence with that. It can be visually seen from the Ra values that the CZT wafer polished with RmSiO_2 abrasives realizes more precision surface compared with that using mSiO_2 and sSiO_2 spheres, implying that the as-synthesized RmSiO_2 abrasives have greater surface machinability than mSiO_2 and sSiO_2 spheres. Moreover, the surface smoothness achieved by RmSiO_2 -1 is the highest, revealing its superiority in ultra-precision manufacturing.

Since the roughness values cannot describe the spatial variation at the same horizontal line, they may be misled by mutational peak or valley values, while the profile of the cross-sectional lines may indicate it well. Therefore, the section lines were derived from AFM 2D height images of CZT_{R1} , CZT_{R2} , CZT_{R3} , CZT_{m} , and CZT_{s} wafers along central dotted lines, as presented in Fig. 5g. The measured peak to valley (PV) values of their profiles were determined to be 1.36, 2.24, 1.74, 2.82, and 2.85 nm, respectively. Both the gentlest fluctuation and smallest PV value of profile taken from the image of CZT_{R1} wafer indicate the reduced topography variations and improved surface quality achieved by RmSiO_2 -1 abrasives. Furthermore, the AFM 3D images (Fig. 5h–l) give a more intuitive view of their topographies. As noticed, the surface undulation is characterized obviously in images of CZT_{R2} , CZT_{m} , and CZT_{s} wafers (Fig. 5i, k, l), and an evident pit can be observed on the CZT_{R3} wafer surface (Fig. 5j). This is the reason why they have higher Ra values, and perhaps the poorer surface quality is resulting from some indentations of embedded sSiO_2 , mSiO_2 , and RmSiO_2 particles with large size or stiffness.

According to the theoretical, experimental and simulated literature reports, it is widely believed that porous abrasives present more softness and elasticity than solid

Figure 5 AFM 2D images (a–e) and corresponding 3D images (h–l) of CZT wafers polished with different abrasives: (a, h) RmSiO₂-1; (b, i) RmSiO₂-2; (c, j) RmSiO₂-3; (d, k) mSiO₂; (e, l) sSiO₂. (f) Rough values of polished CZT wafers and (g) height comparison of section lines.

abrasives. Therefore, due to the non-rigid character, porous abrasives will deform elastically in the interfacial contact process between the polishing pad and CZT wafers, compared with sSiO₂ spheres when loads are applied. The elastic deformation of porous abrasives could reduce the plough behavior of abrasives to wafers, contributing to surface planarization and damage elimination. Thus, it can be explained reasonably that the polishing qualities of CZT_{R1}, CZT_{R2}, CZT_{R3}, and CZT_m are better than that of CZT_s wafers.

In addition, the most smooth and non-destructive surface obtained by RmSiO₂-1 rather than RmSiO₂-2 and RmSiO₂-3 can also be interpreted by this elastic deformation mechanism from the interfacial contact area. HRSEM, XRD and N₂ adsorption/desorption isotherm measurements further verified that the RmSiO₂ particles with different *L/d* ratios have diverse pore frameworks. Moreover, it was verified that the *E* value of RmSiO₂-1 abrasives is the lowest because of their well-ordered and abundant porous structure through modulus measurements. On the basis of elastic micro-contact mechanics, the furthest deformation of RmSiO₂-1 will occur among the RmSiO₂ when loading pressure because of its smallest *E* values. Therefore, the indentation and penetration

depths also diminish accordingly, inducing low surface defects and high quality. Furthermore, both the smaller size and compacter porous structure of RmSiO₂-1 decrease the density per single particle, and thus the total number of RmSiO₂-1 particles between the contact of CZT wafers and polishing pad will increase with the constant abrasive solid content in polishing slurry. A large number of active RmSiO₂-1 particles play a dominant role in dispersing pressure even the contact area of single large-sized RmSiO₂-2 or RmSiO₂-3 particles is much larger with wafers. Therefore, the pressure per particle loaded on RmSiO₂-1 is much lower than that polished with RmSiO₂-2, and RmSiO₂-3. This is another reason for indentation reduction and surface planarization on CZT_{R1} wafers. As discussed above, compared with RmSiO₂-2 and RmSiO₂-3, RmSiO₂-1 with abundant pores is more elastic and softer, contributing to lower topography variations and flatter surface.

Moreover, MD simulation results provided insightful evidence that the movement pattern of ellipsoidal shaped abrasives will transform from rolling to sliding with increasing *L/D* ratio, which contributes to the reduction of surface defects (e.g., groove depth, dislocation length) [26,27]. For RmSiO₂ abrasives, these particles are at-

tempted to slide between the CZT wafers and polishing pad because of their well-designed rod shape. As a result, the sliding probability of RmSiO₂-3 abrasives was maximum, while mSiO₂ abrasives tend to adopt the rolling behavior with generating pits and ravines. Probably, this can explain why RmSiO₂ abrasives achieve more precision machining than mSiO₂ ones.

Furthermore, the used RmSiO₂-1 abrasives (RmSiO₂-1-used) were characterized to speculate the deformation of abrasives after the CMP process. The morphology and porous information of RmSiO₂-1 abrasives before and after the CMP process are shown in Fig. 6. The TEM and SEM images (Fig. 6a, b, e, f) show that some impurities, dirtiness and fragments appear over the RmSiO₂-1-used abrasives with a few broken particles. More obviously, the diameter of abrasives became smaller (loss of 16%) and the length became shorter (loss of 10%) after the CMP process. Primarily, the change of dimensions can indicate the abrasives deform and wear away under the action of applied forces. Once the force beyonds the maximum loading, the deformation mode of particles will change from elastic to plastic with the formation of the fragmentation. Secondly, the dimension reduction in diameter direction is visibly higher than that in length direction, implying the dominating stress-bearing surface of abrasives is their largest cylindrical surface. However, for spherical mSiO₂ abrasives, the force and pressure are

always applied at a random point on their spherical surface. Compared with a large area of stress-bearing surface, the contact mode by point is more inclined to generate pits and scratches, which is not conducive to surface planarization. This is the reason why RmSiO₂ abrasives realize more precision machining than mSiO₂ abrasives even though they have the similar mesoporous structure.

Additionally, the pore nature of RmSiO₂-1 and RmSiO₂-1-used abrasives was also characterized. The small-angle XRD patterns (Fig. 6k) suggest that the peak intensity of RmSiO₂-1-used abrasives becomes weaker than that of the RmSiO₂-1 abrasives. This demonstrates their order degree of mesostructure decreases during the CMP process, which may result from the collapse and destruction of dense porous structure on RmSiO₂-1 abrasive surface. Due to the channel collapse, the pores expand and the number of pores with larger diameter increases as demonstrated in Fig. 6l (inset). For this reason, although the average pore diameters of RmSiO₂-1 and RmSiO₂-1-used abrasives are both about 2.4 nm, the surface area of RmSiO₂-1-used abrasives is 934 m² g⁻¹, which is slightly lower than that of RmSiO₂-1 abrasives (1066 m² g⁻¹). The variation of the pore character manifests the significant role of mesoporous structure in alleviation of external pressure to CZT wafers by means of self-disintegration.

Figure 6 (a) TEM and (b) SEM images of RmSiO₂-1 abrasives and their (c) length and (d) diameter distributions. (d) TEM image, (e) SEM image, the corresponding magnified (i) TEM and (g) SEM images of RmSiO₂-1-used abrasives, and their (g) length and (h) diameter distributions. (k) Powder small-angle XRD patterns and (l) N₂ adsorption/desorption isotherms of RmSiO₂ and RmSiO₂-1-used abrasives.

Another critical index for CMP performance is the polishing efficiency, which can be digitized to MRR. The MRRs of CZT_{R1}, CZT_{R2}, CZT_{R3}, CZT_m, and CZT_s wafers are determined as 8.25 ± 0.84 , 8.72 ± 0.71 , 8.81 ± 0.86 , 7.52 ± 0.84 , and $9.35 \pm 0.78 \mu\text{m min}^{-1}$, respectively. It can be concluded that the sSiO₂ spheres achieve the highest efficiency, but just a little higher in the removal of CZT than RmSiO₂ abrasives in the CMP process, and the removal rate of mSiO₂ is the lowest. For RmSiO₂ abrasives, the calculated MRR results indicate the polishing efficiency of RmSiO₂-1 is slightly low, and the polishing speed of the most efficient RmSiO₂-3 is just a little higher than that of RmSiO₂-2. The reasons for this are complicated and can be explained legitimately by the following four theories.

Above all, contact area-based models were proposed in the literature and recognized extensively [62,63]. Chen *et al.* [20] investigated the abrasives' mechanical wear effect for material removal in the CMP process, and Equation (2) calculating the MRR in contact state is provided as follows:

$$\text{MRR}_{\text{contact}} = d\delta U, \quad (2)$$

where d is the actual contact radius of abrasives, δ is the penetration depth and U is the rotation speed of polishing pad. As presented in the equation, the MRR is in direct proportion to d and δ when U is kept as a constant. Due to the rigid nature, sSiO₂ spheres scarcely deform when they are in contact with CZT wafers, while RmSiO₂-2 and RmSiO₂-3 abrasives will perform low elasticity deformation. Their d and δ values are both larger than those of RmSiO₂-1 abrasives, and accordingly their polishing speed is higher than that of RmSiO₂-1 and the efficiency of sSiO₂ is the highest deservedly because of its lowest E . In addition, the actual contact area between the abrasives and CZT wafers can directly affect the MRR, too. The contact area of RmSiO₂-2 and RmSiO₂-3 increases inevitably with their larger size compared with RmSiO₂-1, and that of RmSiO₂-3 is the largest because of its micron size. This is the reason why RmSiO₂-3 is the most efficient abrasive. The evidence is that the polishing speed of RmSiO₂-1 towers over the speed of mSiO₂ even though they have a similar size and porous structure. Furthermore, we know that the distinction of the contact mode causes this speed difference. RmSiO₂-1 abrasives realize the material removal through line contact with CZT wafers, while the contact manner of mSiO₂ is the point due to its spherical shape. Then, driven by the flowing slurry, the abrasives would move and rotate, resulting in the actual contact area of RmSiO₂-1 and mSiO₂ changing

into a 2D surface and 1D line, respectively. The difference in contact area leads RmSiO₂-1 abrasives to achieve higher efficiency than mSiO₂. Moreover, the transition from sliding to rolling would decrease the friction coefficient of abrasives dramatically. Therefore, the friction force of mSiO₂ abrasives was lower than that of RmSiO₂ ones with the fixed stress. Accordingly, the less material removal amount per unit time of mSiO₂ abrasives results in their poor polishing speed. Moreover, the friction diagram between ellipsoidal abrasives and substrates proposed by Dong *et al.* [25] also verifies it.

Furthermore, compared with sSiO₂ abrasives, the RmSiO₂-1 shows a mesoporous structure that is conducive to raising its polishing speed. It was reported that porous abrasives present a special removal mechanism for materials, which is mainly related to their pore size and structure. For example, Chen *et al.* [64] uncovered the mechanical effect of porous silica clusters on substrates and their pore size-dependent polishing behavior by means of MD simulations. The results revealed that the high MRR is caused by the combined effect of the plough, adhesion, and permeation of clusters to substrate atoms. The adhesion effect plays a dominant role in material removal. It is worth mentioning that the enlarged pore size of clusters will result in increasing active contact area and enhanced adhesion of the pore to substrate atoms. Thus it is easier for abrasives with large-sized pores to pull off the polished material. For the as-synthesized abrasives, RmSiO₂-1 has more large-sized pores than RmSiO₂-2 and RmSiO₂-3 quantitatively, which was confirmed by BJH pore diameter distributions. Therefore, the large number of expanding pores on the RmSiO₂-1 surface facilitates the adhesion and pulling effects of abrasives to CZT wafers, eventually leading to relatively not too low MRR.

Furthermore, Mo *et al.* [52] hold the view that elastic deformation also results in the adhesion effect, and plays a significant role in friction wear at the nanoscale. This theory is also in favor of understanding why the MRR of RmSiO₂-1 is not too low. It is all because of its highest E .

Last but not least, as we know, the CMP performance depends on the balance between chemical and mechanical effects. For a chemical reaction, Qi *et al.* [65] reported that mesoporous abrasives can store water in their micropores, increasing their chemical activity in the CMP process. According to the BJH pore volume results, the RmSiO₂-1 has the largest pore volumes due to its abundant micropores. Therefore, the RmSiO₂-1 presents a strong slurry storage capacity, which contributes to an active tribo-chemical reaction. This may be the other

reason that the MRR of RmSiO₂-1 is slightly lower than those of RmSiO₂-2 and RmSiO₂-3. Moreover, the contact angle measurement (Fig. S6) also provides powerful evidence that RmSiO₂-1 is more hydrophilic, which will result in better dispersibility and polishing efficiency.

For evaluating the CMP stability of RmSiO₂ abrasives, the identical CMP experiments with the RmSiO₂-1 were performed three times as shown in Fig. S7. The 2D and 3D images (Fig. S7a–h) present that the CZT wafers after the identical CMP tests present the same relatively homogeneous color distribution with the original CMP results. Moreover, the corresponding *Ra* values calculated by their height data of CZT wafers after the 1st, 2nd, and 3rd repeated test are 0.231, 0.226, and 0.194 nm, respectively, which are even lower than the original *Ra* values. Moreover, the *Ra*_{average}, *Rq*_{average} and the peak-to-valley values of section lines derived from AFM 2D images all keep nearly the same variation trend with the lowest *Ra* values. This demonstrates that the RmSiO₂-1 abrasives can keep the ultra-precision machining ability steadily. Besides, the polishing speed of the repeated tests are 7.98 ± 0.83 , 8.05 ± 0.86 , and $7.90 \pm 0.89 \mu\text{m min}^{-1}$, respectively, which are broadly in line with the original MRR value. Therefore, it can be considered that the CMP performance achieved by RmSiO₂ abrasives is stable with valuable practical application.

Interfacial mechanochemistry in CMP process

It is well known that the ultra-precision surface machining with high efficiency in CMP process is achieved through a synergistic effect of chemical corrosion and mechanical removal. Moreover, the speculation that the chemical reactivity is induced or driven by mechanical behavior mainly in the form of force, kinetic energy, and frictional heating becomes increasingly acknowledged in mechanochemical reactions [66–68]. On the one hand, the solid substrate subjected to mechanical stress could initiate the irreversible plastic deformations of convexes on its surface, such as shearing and twisting, and convert to kinetic energy. This will result in structural collision and morphology transition of solid materials. On the other hand, the mechanical kinetic energy could generate plentiful friction heating to accelerate the molecular movement and induce the chemical reaction [69,70]. Similarly, this mechanochemical mechanism also applies to the CMP process. For example, as previously reported by utilizing MD simulation, the oxidation of the substrate surface is mechanically induced at the friction interface [23]. The mechanical shearing and sliding behavior of abrasive grain play a key role in the intrusion of O atoms

and raising of the substrate atoms, ultimately resulting in dissociation of surface chemical bonds. Therefore, we ratiocinate boldly that the chemical corrosion in the CMP process can be mechanically induced by importing frictional momentum and heating of abrasives.

With the sustaining input of mechanical energy, chemical compositions in slurry are activated and the chemical reactions between slurry and substrates proceed spontaneously. After being modified by slurry, the substrate will present an easy-to-remove state, which is in favor of achieving surface planarization. Therefore, besides the mechanical character of abrasives, the chemical properties of slurry are equally crucial to CMP performances. It is necessary to figure out the chemical effect of each composition in slurry and further reveal the chemical reaction on interface contacts.

Primarily, electrochemical tests were performed to analyze the CZT corrosion rates of the polishing slurry. The corrosion rate can be evaluated by passivation current density calculated from Tafel polarization curves (Fig. S8). The smaller density signifies the test solution with higher corrosivity to CZT substrates. According to the calculated results, PEG2000 solution has the lowest passivation current density, followed by H₂O₂, SiO₂, TA solution, and the polishing slurry has the highest value. The CZT corrosion rate of PEG2000 is even lower than that of SiO₂, which indicates that PEG2000 has no erosive attack on CZT substrates during the CMP process. Moreover, it is interesting to note that H₂O₂, a typical oxidizing agent, exhibits much lower corrosive speed. This is because the corrosivity of H₂O₂ is so strong that a dense oxidation layer would be formed immediately to obstruct the charge exchange once dipping the CZT substrate into the H₂O₂ solution. Therefore, the H₂O₂ among these ingredients still acts as an oxidizing agent to corrode the CZT surface in spite of its small current density. However, the corrosion rate of polishing slurry including H₂O₂ is not affected by its strong oxidizability and remains high. This is because that the TA plays an etching role. As long as the oxidation layer is formed, the H⁺ ionized by TA would react with metallic oxide and collaborate with abrasives to achieve the removal of the oxidation layer integrally and make the new flat CZT surface exposed. Thus, TA can be regarded as a pH adjuster to provide an acidic environment for easier mechanical removal of the oxide layer. Moreover, the Tafel polarization curve of TA is similar to that of the polishing slurry, which confirms TA has a promoted effect on CZT corrosion.

In order to further characterize the chemical properties

of polishing slurry, the XPS spectra were scanned to detect the chemical states of Te, Cd, and O elements on the CZT wafer surface. The amount of Zn element is too little to monitor, and thus its analysis was neglected. The XPS spectra of the CZT substrate after lapping and polishing are shown in Fig. 7. The core level peak near 572 eV has been identified as the Te^{2-} ions in the CZT with a perfect zincblende structure [71]. Thus, the peaks located at 572.2 eV are attributed to Te–Cd or Te–Zn bonds in CZT. Moreover, another component peak at 572.9 eV in the spectrum of polished CZT can be ascribed to $\text{Te}^0 3d_{5/2}$ for the metallic state, while the peak at 572.4 eV in the spectrum of CZT after lapping represents Te with a certain valence state between 0 and -2 , which may be caused by slight oxidation in the high-speed lapping process. In addition to this, the peak located at 575.8 eV can be ascribed to Te^{4+} –O bonds in tellurium compounds such as TeO_2 , TeO_3^{2-} , and $\text{Te}_2\text{O}_5^{2-}$. It is well known that atoms at higher oxidation states will exhibit higher binding energy [72], so the individual small peak at 576.9 eV in the spectrum of polished CZT can be assigned to Te^{6+} –O bonds with a higher valence state. Comparing the Te $3d_{5/2}$ spectra of CZT before and after lapping and polishing, it can be noted that the peaks attributed to Te^{4+} –O bonds become significantly stronger and the peaks accredited to the low valence state become weaker. Moreover, the spectrum of polished CZT exhibits a small peak with a high valence state. All of this is because that CZT wafers are oxidized by H_2O_2 after CMP. The reactive Equations (3)–(5) of H_2O_2 solution on CZT wafer surface are proposed as followed:

For $\text{Cd}_{5/2}$ spectra of CZT wafers after lapping and polishing (Fig. 7b, e), the peaks located at 404.8 and 404.9 eV can be attributed to Cd linked to Te in CZT and Cd–O bonds existing in CdO, respectively. Moreover, the peak intensity in the spectrum of polished CZT is obviously weaker than that of CZT after lapping, which may be caused by TA. After oxidation by H_2O_2 , the cadmium oxide will be formed in quantity, and the original Cd–Te bonds on the CZT surface will be reduced accordingly. However, the H^+ ionized by TA will react with the basic metal oxides and the generated Cd^{2+} will be dissolved in the slurry. The relevant chemical reactions are depicted by Equation (6) as below:

In addition to this, TA, as one of the natural polyphenols, can be deprotonated and then chelate with metal ions through its rich catechol groups to form metal-phenolic complexes [73,74]. The chelate of TA with dissociated Zn^{2+} or Cd^{2+} in the polishing slurry can be observed in the FTIR spectrum. As shown in Fig. 8a, the emerging adsorption bands at 1715, 1196 and 1085 cm^{-1} in the chelate of TA and CZT (TA–CZT) derive from the stretching vibration of the carbonyl group (C=O), phenolic hydroxyl group (Ar–OH), and carbon–oxygen bond (C–O) of TA molecule, respectively [75–77]. This substantiates the successful chelation between TA and dissociated metal ions in polishing slurry, which will reduce the direct emission of Zn^{2+} or Cd^{2+} and protect the environment. Moreover, their complexation state is in a highly pH-dependent manner [78,79]. Under the acidic polishing condition, one metal ion can only chelate with one catechol group in deprotonated TA, and their chelating interactions are shown in Fig. 8b.

Figure 7 XPS spectra of Te 3d (a, d), Cd 3d (b, e) and O 1s (c, f) core levels on CZT wafers subjected to different treatments: after lapping (a–c), after CMP (d–f).

Besides, the O 1s peaks in XPS spectra (Fig. 7c and f) are divided into three components located at 530.0, 531.9, and 533.7 eV, corresponding to CZT oxide, C–O bonds, and loosely adsorbed H–O bonds on the CZT surface, respectively. As we can see, the intensities of the former two components are enhanced strongly after CMP. This is most probably because of the adsorption of PEG2000 with long chains of molecules and TA with plentiful hydroxyl groups on the CZT surface.

To further support these inferences about the chemical properties of ingredients in the polishing slurry, XPS spectra of CZT wafers immersed in solutions including different ingredients are recorded in Fig. S9. According to the position and valence state of each component derived from Te 3d_{5/2} and Cd 3d_{5/2} peaks in Fig. 7, it can be inferred that the corresponding valence states of components in Fig. S7 have similar positions with them. As observed, the peak of Te 3d_{5/2} with high oxidant valence state in intensity order from strong to weak belongs to CZT wafers immersed in the polishing slurry, H₂O₂, TA, and PEG2000 solutions, respectively. Moreover, the peaks assigned to cadmium oxide in Cd 3d_{5/2} spectra also follow this pattern. This is in line with that H₂O₂ exhibits strong corrosivity properties to act as an oxidizing agent in the polishing slurry. For spectra of CZT wafers immersed in the polishing slurry, the peaks accredited to the original CZT state are the weakest, but the peaks ascribed to CZT oxide are not the strongest even though the slurry contains H₂O₂. This confirms the previous speculation that the H⁺ ionized by TA will react with CZT oxide and accelerate the oxidation process through the “forming and removing oxide layer” cycle. Furthermore, the weak oxidizing effect can be noticed in the spectra of CZT wafers immersed in TA, indicating that only TA does not play a prominent oxidizing role yet still has a feeble corrosion effect on CZT wafers. The peak attributed to

the oxidizing state in spectra of CZT wafer immersed in PEG2000 solution almost has no obvious peak, which corroborates that PEG2000 has no corrosion damage effect on CZT wafers. The PEG2000, a linear polymer with amphiphilic property, is widely used as non-ionic surfactants in foodstuff, cosmetics, and pharmaceutical industries due to its inertness and biocompatible nature. The primary function of PEG2000 in polishing slurry is to utilize its oxygen groups to link to hydroxyl groups on silicon particle surface *via* hydrogen bonds. After modification with PEG2000, the resultant silica particles will repel each other by steric effects and exhibit excellent colloidal stability [80–82].

Up to this point, the chemical property of every component in the polishing slurry, and the reaction occurring during the CMP process have been discussed and identified. Thereby, the CMP mechanism of the developed polishing slurry containing novel RmSiO₂ abrasives to CZT wafers can be elucidated into three steps, as shown in Fig. 9. Originally, with the actuation of the exterior loads and kinetic energy, RmSiO₂ abrasives move quickly and rub against CZT substrates, causing the bulge of the impact to collapse and generating frictional heating. This mechanical effect accelerates the molecular motion of chemical components in the slurry and induces a series of following chemical reactions: firstly, H₂O₂ solution in the slurry acting as an oxidizing agent will oxidize rugged CZT surface to form a compact oxidized layer. Then, the H⁺ released by ionization of TA will react with the basic metal oxides such as CdO and ZnO into metal ions, causing the removal of the partially oxidized layer. Subsequently, the deprotonated TA molecules chelate with the Cd²⁺ and Zn²⁺ to form a catechol–Cd²⁺/Zn²⁺ mono-complex with a stoichiometric ratio of 1:1. Lastly, the complexes are discharged as the flowing polishing slurry. In the end, dispersed RmSiO₂ abrasives will deform

Figure 8 FTIR spectra of TA-CZT and TA (a), the chelating process for catechol–Cd²⁺/Zn²⁺ mono-complex under acid condition (b).

Figure 9 Proposed schematic diagram of CMP mechanism induced by the developed novel slurry.

elastically when subjected to the extrusion of the polishing pad and CZT wafers due to their abundant pores with a well-ordered structure and accurately remove the remaining oxidized layer. The reduction of indentation depth contributes to the formation of a low-defect surface. After several of these CMP cycles, the surface accuracy of CZT wafers achieves the sub-nanometer scale ultimately.

CONCLUSIONS

In conclusion, an extended Stöber method has been adapted to successfully synthesize a series of non-spherical RmSiO₂ particles with controllable sizes and diverse mesostructures, which were eventually applied in a sustainable CMP process on CZT wafers. The polishing results indicate that the non-spherical mesoporous RmSiO₂ abrasives can achieve a substantial improvement of surface planarization to soft and brittle materials relative to commercial silica gel, mSiO₂ and sSiO₂ spheres. Furthermore, on account of the well-ordered and tightly arranged mesoporous structure on RmSiO₂ abrasive surface, they have lower E values and deform elastically when loading is applied, which results in the low topographical variation and defect-free surface. Moreover, their specific compact pore structure is prone to generating large-sized pores to adhere to and pull off materials and storage slurry to accelerate the interfacial chemical reactions in the CMP process, which facilitates the improvement of material removal speed. In addition, the rod shape of RmSiO₂ can enhance the actual contact

area between abrasives and CZT wafers, and increase its friction coefficient by sliding movement, consequently raising the polishing efficiency. Ultimately, the “mechanically inducing-chemical corrosion-mechanical removal” cyclic model is proposed to describe the synergistic mechanochemical effect of mechanical friction from RmSiO₂ and chemical corrosion from other compositions in the CMP process. This work reveals a possible CMP mechanism for CZT materials and will provide guidance on precision machining for other key materials and components.

Moreover, as abrasives are the primary participant in mechanical energy transmission and chemical reaction, their physicochemical properties are an important factor in CMP performance. With the increasing demand for more ultra-precision and the more non-damage surface of core materials, it is suggested to optimize the characters of abrasives, such as their morphology, structure, and even surface chemical state. More importantly, the CMP performance could be improved by individually or jointly modifying the abrasive properties. Therefore, it is imperative to propose more synthetic strategies of modified abrasives or novel recipes in polishing slurry to promote the development of CMP technology.

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Author contributions Zhang Z and Liu J conceived this project. Liu T guided the experiments. Gao P and Meng F performed the experiments and analyzed the CMP mechanism. Gao P wrote the manuscript and Ye RP revised it. All authors discussed the results and commented on the manuscript. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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介孔结构非球形磨粒的制备及其在化学机械抛光中的应用研究

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摘要 化学机械抛光技术通过抛光液中化学试剂的化学腐蚀和纳米磨粒的机械磨削双重耦合作用, 在原子水平上去除材料表面缺陷, 实现全局平坦化表面加工, 现已成为关键零部件和器件材料的超精密表面制造的关键手段. 在化学机械抛光加工中, 纳米磨粒是外加机械能向抛光系统输入和转化的媒介. 磨粒的机械性能很大程度上影响着化学机械抛光加工过程中机械作用的强弱, 决定着加工性能的优劣. 本文主要针对碲锌镉晶体的软脆难加工特性, 对传统实心球形磨粒进行了结构和形貌的双重改性, 合成了一系列长径比可控、介孔结构排列有序的棒状二氧化硅磨粒. 与商用硅溶胶、实心及介孔二氧化硅球形磨粒相比, 棒状介孔磨粒由于其类弹簧多孔结构和大尺寸接触面积, 在化学机械抛光实验中展现出优异的弹性变形能力和高质高效超精密表面加工能力. 此外, 通过分析X射线光电子能谱和其他表征结果, 本文对所提出的绿色环保化学机械抛光液在碲锌镉晶体化学机械抛光加工中的潜在作用机理进行了说明, 这将为改善磨粒的切削性和难加工材料的精密制造提供新的策略.