


Cite this: *RSC Adv.*, 2024, 14, 29559

# Interaction mechanism of Al<sub>2</sub>O<sub>3</sub> abrasive in tantalum chemical mechanical polishing

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Al<sub>2</sub>O<sub>3</sub> abrasive is expected to enhance chemical mechanical polishing (CMP) efficiency compared to the SiO<sub>2</sub> abrasive. However, Al<sub>2</sub>O<sub>3</sub> powder has dispersion issues and the material removal mechanism by Al<sub>2</sub>O<sub>3</sub> remains unclear. This study investigated the role of Al<sub>2</sub>O<sub>3</sub> abrasive in the tantalum CMP. It is revealed that (NaPO<sub>3</sub>)<sub>6</sub> can effectively disperse Al<sub>2</sub>O<sub>3</sub> powder in water. PO<sub>3</sub><sup>−</sup> improves the stability while Na<sup>+</sup> deteriorates it. The total Na<sup>+</sup> concentration should be lower than the turning point to attain high stability. With stable Al<sub>2</sub>O<sub>3</sub>-containing slurries, a relatively high material removal rate of tantalum can be obtained at an alkaline pH. The characterization results indicate that the Ta element can be adsorbed on Al<sub>2</sub>O<sub>3</sub> probably due to the chemical interaction between Al<sub>2</sub>O<sub>3</sub> and the tantalum surface. Moreover, the Al<sub>2</sub>O<sub>3</sub> microsphere tip starts to remove tantalum at 0.48 GPa, which is much lower than the yield strength of the tantalum surface film. For the mechanism, tantalum can be oxidized by H<sub>2</sub>O<sub>2</sub> at alkaline pH. When Al<sub>2</sub>O<sub>3</sub> presses and slides on the tantalum surface, tribochemical reactions occur, forming a chemical bond of Al–O–Ta at the interface. As Al<sub>2</sub>O<sub>3</sub> moves, the bond is stretched and tantalum is detached. The findings provide mechanistic insight into Al<sub>2</sub>O<sub>3</sub> abrasive in CMP.

Received 21st May 2024  
Accepted 19th August 2024

DOI: 10.1039/d4ra03743j

rsc.li/rsc-advances

## 1 Introduction

Tantalum/tantalum nitride has been widely used as the barrier layer for copper interconnect in integrated circuits (IC) because it can prevent copper diffusion and has good adhesion with copper and the dielectric.<sup>1</sup> In the dual-damascene process for fabricating copper interconnect, tantalum/tantalum nitride will be polished in the P3 stage of chemical mechanical polishing (CMP) to achieve local and global planarization, enabling the subsequent photolithography.<sup>2</sup> With the rapid development of IC, it is important to continuously improve the CMP performance of tantalum (tantalum nitride is quite like tantalum in terms of CMP) such as the CMP efficiency.

Tantalum CMP can be considered a nanoscale corrosive wear process, which is mainly affected by the interaction between the tantalum surface and abrasive.<sup>3–5</sup> Therefore, abrasive plays a critical role in the tantalum CMP. At present, SiO<sub>2</sub> is primarily used in the tantalum CMP. Li *et al.*<sup>4,6</sup> used several types of SiO<sub>2</sub> with different specific surfaces to polish tantalum. It was revealed that the tantalum material removal rate (MRR) increases with the specific surface of SiO<sub>2</sub> increasing. This may

be because a larger specific surface possesses a higher Si–OH content on the SiO<sub>2</sub> surface, resulting in more intensive chemical interaction between the tantalum surface and SiO<sub>2</sub>. Li *et al.*<sup>7</sup> used SiO<sub>2</sub> with different hydroxyl contents to polish tantalum. The experimental results showed that the tantalum MRR is linearly proportional to the hydroxyl content on the SiO<sub>2</sub> surface. In addition, a large amount of tantalum is found on the SiO<sub>2</sub> surface after polishing using atomic absorption spectrophotometry. It was concluded that a strong chemical interaction exists between tantalum and hydroxyl groups on the SiO<sub>2</sub> surface. Vijayakumar *et al.*<sup>8</sup> put forward the polishing mechanism of tantalum by SiO<sub>2</sub>. Hydroxyl groups on the SiO<sub>2</sub> surface can react with tantalum to form Si–O–Ta bonds. As SiO<sub>2</sub> moves, the bonds are mechanically torn, leading to the removal of tantalum.

Researchers also used Al<sub>2</sub>O<sub>3</sub> as the abrasive in the tantalum CMP. Li *et al.*<sup>6</sup> compared the polishing performance of Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in the tantalum CMP. The experimental results showed that Al<sub>2</sub>O<sub>3</sub> can achieve a higher tantalum MRR than SiO<sub>2</sub>. Li *et al.*<sup>7</sup> revealed that not only the hardness of the abrasive and the tantalum surface but also the hydroxyl group on the abrasive surface affects the tantalum removal. When using Al<sub>2</sub>O<sub>3</sub> with different bulk densities to polish tantalum, Al<sub>2</sub>O<sub>3</sub> with a higher bulk density can attain a higher tantalum MRR. This is because an increased hydroxyl content on Al<sub>2</sub>O<sub>3</sub> results in stronger interaction between Al<sub>2</sub>O<sub>3</sub> and the tantalum surface.

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Compared to the commonly used  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  is expected to enhance the CMP efficiency further. However, the interaction mechanism between  $\text{Al}_2\text{O}_3$  and the tantalum surface has not been investigated in-depth. Moreover, based on our preliminary tests,  $\text{Al}_2\text{O}_3$  powder has a dispersion issue in water, hindering the development of  $\text{Al}_2\text{O}_3$ -containing slurries. Therefore, this study first used an effective dispersant  $(\text{NaPO}_3)_6$  to disperse  $\text{Al}_2\text{O}_3$  powder in ultrapure water. Then, stable  $\text{Al}_2\text{O}_3$ -containing slurries were prepared, and their polishing performance was studied. Afterward, transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), and first-principles calculation were performed. Based on the experimental results, the role of  $\text{Al}_2\text{O}_3$  abrasive in the tantalum CMP was revealed. The findings provide new insights into the material removal mechanism of tantalum in CMP.

## 2 Experimental details

$\text{Al}_2\text{O}_3$  powder (AEROXIDE Alu C, purchased from Evonik Industrial AG) was used as the abrasive. Sodium hexameta-phosphate  $((\text{NaPO}_3)_6)$  was used as the dispersant to disperse  $\text{Al}_2\text{O}_3$  powder in ultrapure water, preparing an  $\text{Al}_2\text{O}_3$  suspension.<sup>9</sup> Specifically,  $(\text{NaPO}_3)_6$  was first dissolved in ultrapure water. Then,  $\text{Al}_2\text{O}_3$  powder was added under continuous stirring. Afterwards, the  $\text{Al}_2\text{O}_3$  suspension was stirred for 1 h and sonicated for 15 min. Finally, if necessary,  $\text{NaNO}_3$  was added to the  $\text{Al}_2\text{O}_3$  suspension to provide  $\text{Na}^+$  and control the total  $\text{Na}^+$  concentration. To characterize the long-term stability of the  $\text{Al}_2\text{O}_3$  suspension, it was allowed to stand for 24 h, and then the turbidity values of the upper layer and the bottom layer of the suspension were measured with a turbidity meter (WZS-188, Shanghai Yidian Scientific Instrument Co., Ltd.). After obtaining a relatively stable  $\text{Al}_2\text{O}_3$  suspension, tantalum CMP slurries were prepared by adding additional  $\text{H}_2\text{O}_2$  and adjusting pH (dilute  $\text{NaOH}$  and  $\text{HNO}_3$ ). All the above chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.

In the CMP experiments, a tantalum disk (50.8 mm diameter, 99.99% purity, China New Metal Materials Technology Co., Ltd.) was polished on a benchtop polisher (UNIPOL-1200S, Shenyang Kejing Auto-Instrument Co., Ltd.). Table 1 shows the CMP process conditions. During polishing, the CMP slurry was stirred continuously to maintain excellent dispersion. The weights of the tantalum disk before and after polishing were measured with a microbalance (0.01 mg readability, MSA225S, Sartorius). The MRR was calculated with the weight loss method.<sup>10</sup> In particular, the density of tantalum is

$16.68 \text{ g cm}^{-3}$ .<sup>11</sup> The topographies and surface roughness  $S_a$  of the tantalum disk after polishing were measured with an optical surface profiler (SuperView W1, Chotest). The scan area was  $97.9 \mu\text{m} \times 97.9 \mu\text{m}$ . Each CMP slurry was repeated four times.

To explore the interaction between  $\text{Al}_2\text{O}_3$  and tantalum, the CMP slurry was used 1 time, 10 times repeatedly and 20 times repeatedly, and then collected after polishing. The topography and compositional distribution of  $\text{Al}_2\text{O}_3$  abrasive in the recycled slurry were characterized with TEM (Talos F200X, FEI) and EDS.

In order to investigate the interaction between  $\text{Al}_2\text{O}_3$  and tantalum surface further, the adhesion force between an  $\text{Al}_2\text{O}_3$  microsphere tip ( $2.5 \mu\text{m}$  nominal radius. The AFM probe was purchased from Novascan Technologies, Inc. It had a spring constant of  $14.08 \text{ N m}^{-1}$  calibrated by the thermal noise method<sup>12</sup>) and the tantalum surface was measured in the designated solution on an atomic force microscope (MFP-3D, Asylum Research). The dwell time was varied. The experimental conditions were as follows:  $1 \mu\text{m}$  distance,  $500 \text{ nm s}^{-1}$  velocity,  $0.5 \mu\text{N}$  applied load, and 0 s/5 s/10 s dwell time.

Moreover, AFM wear experiments were carried out to simulate the tantalum material removal process by the  $\text{Al}_2\text{O}_3$  abrasive in CMP on another atomic force microscope (E-sweep, Hitachi). An  $\text{Al}_2\text{O}_3$  microsphere tip was rubbed against the tantalum surface in the designated solution. The applied load was varied. The experimental conditions were as follows:  $0.1 \mu\text{N}/0.2 \mu\text{N}/0.4 \mu\text{N}/0.6 \mu\text{N}/0.8 \mu\text{N}$  applied load,  $1 \mu\text{m s}^{-1}$  relative sliding velocity,  $2 \mu\text{m}$  relative sliding distance, and 100 reciprocating sliding cycles. After the AFM wear experiments, the topographies of the wear areas on the tantalum surface were scanned with a  $\text{Si}_3\text{N}_4$  probe (MSCT, Bruker) in a vacuum. Moreover, the profile of the  $\text{Al}_2\text{O}_3$  microsphere tip was measured by scanning a grating sample (TGT1, NT-MDT). The scanning result exhibits a reverse image of the  $\text{Al}_2\text{O}_3$  microsphere tip rather than that of the grating sample because the curvature of the microsphere tip is much larger than that of the grating spikes.

To prepare a relatively smooth tantalum surface for the above AFM experiments regarding the adhesion force and wear, a small tantalum sample ( $10 \text{ mm} \times 10 \text{ mm}$ , cut from a complete wafer purchased from SKW, Associates, Inc.) was pre-polished, then cleaned with ultrapure water and dried. The CMP slurry contained ultrapure water, 2 wt% colloidal  $\text{SiO}_2$  (YZ8040, purchased from Shanghai YZ-Lapping Material Co., Ltd.), 0.2 wt%  $\text{H}_2\text{O}_2$ , and at pH 10. Fig. 1 shows the topography and the average cross-sectional profile along the A–B direction.

Table 1 CMP process conditions in this study

Condition	Value
Down force	5.0 kg set pressure displayed on the panel
Carrier speed	60 rpm
Platen speed	60 rpm
Slurry flow rate	$100 \text{ mL min}^{-1}$
Time of each polishing	1 min
Polishing pad	Politex (Dow, conditioned for 30 s with a brush before each polishing)



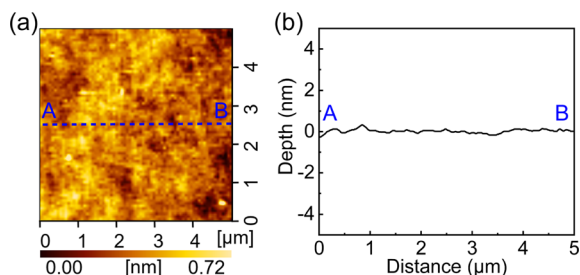


Fig. 1 AFM measurement results of the tantalum wafer surface after polishing. (a) The topography. (b) The average cross-sectional profile along the A–B direction.

As can be seen, after polishing, the tantalum wafer surface is very smooth, meeting the requirement of AFM experiments.

To confirm the interaction between  $\text{Al}_2\text{O}_3$  and tantalum, first-principles calculation based on density functional theory (DFT) was conducted using the Cambridge Sequential Total Energy Package. The exchange-correlation function was described using the generalized gradient approximation of Perdew–Burke–Ernzerhof.<sup>13</sup> The projector-augmented wave potential was used in depicting interactions formed between electrons and ions. The Brillouin zone was sampled using Monkhorst–Pack  $8 \times 8 \times 1$   $k$ -point grids. The calculation parameters for the plane-wave cutoff energy, total energy, and convergence tolerance force were set as 450 eV,  $1 \times 10^{-6}$  eV, and

$0.02 \text{ eV } \text{\AA}^{-1}$  for accurate calculations. The spin interactions were considered, and a 15  $\text{\AA}$  vacuum layer was used to prevent periodic interactions.

## 3 Results and discussion

### 3.1 Stability of $\text{Al}_2\text{O}_3$ suspensions

Stability is a significant indicator of the CMP slurry. Unstable CMP slurry may result in severe defects such as scratches on the workpiece surface after polishing.<sup>14</sup> To this end, this study used  $(\text{NaPO}_3)_6$  to disperse  $\text{Al}_2\text{O}_3$  powder in ultrapure water. Generally, cations, such as  $\text{Na}^+$ , will be introduced to the tantalum CMP slurry unavoidably, for example during adjusting the pH value. Based on the existing research,  $\text{PO}_3^-$  of  $(\text{NaPO}_3)_6$  can improve the stability of  $\text{Al}_2\text{O}_3$ , whereas  $\text{Na}^+$  and other cations may deteriorate it.<sup>15</sup> To explore the stability boundaries of  $\text{Al}_2\text{O}_3$  suspensions under different concentrations of  $\text{PO}_3^-$ , different amounts of  $\text{Na}^+$  (mainly from  $\text{NaNO}_3$ ) were added on purpose. After standing for 24 h, the stability of the  $\text{Al}_2\text{O}_3$  suspension was characterized by measuring the turbidity values of the bottom layer and upper layer of the suspension. If the difference between the two turbidity values (denoted as  $\Delta\text{Turbidity}$ ) fluctuates within a small range of 100–400 NTU and no apparent precipitate appears on the bottom, it suggests that the  $\text{Al}_2\text{O}_3$  suspension is relatively stable; otherwise, it is unstable.

Fig. 2 shows the stability results of the  $\text{Al}_2\text{O}_3$  suspensions. As shown in Fig. 2(a), as the total  $\text{Na}^+$  concentration increases,

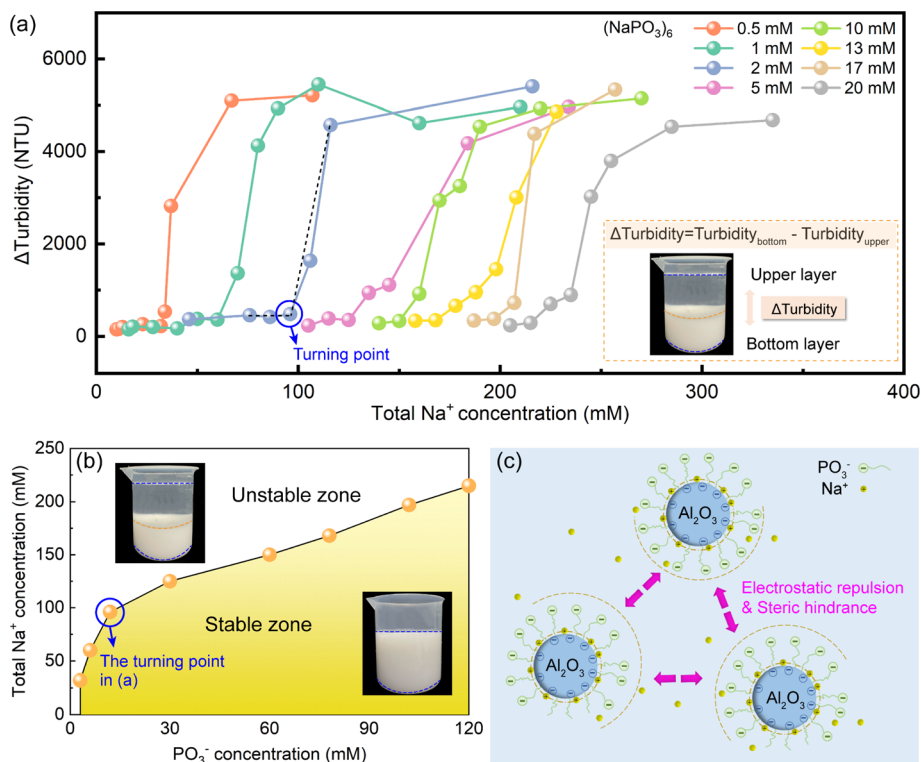


Fig. 2 Stability results of the  $\text{Al}_2\text{O}_3$  suspensions. (a) The effect of the total  $\text{Na}^+$  concentration on the stability of the  $\text{Al}_2\text{O}_3$  suspension. In the experiments,  $(\text{NaPO}_3)_6$  concentrations were set as 0.5 mM, 1 mM, 2 mM, 5 mM, 10 mM, 13 mM, 17 mM, and 20 mM. The abscissa is the total  $\text{Na}^+$  concentration in the  $\text{Al}_2\text{O}_3$  suspension, and the ordinate is  $\Delta\text{Turbidity}$  after letting the  $\text{Al}_2\text{O}_3$  suspension stand for 24 h. (b) The turning points of the total  $\text{Na}^+$  concentration corresponding to different  $\text{PO}_3^-$  concentrations. (c) The dispersion mechanism of  $\text{Al}_2\text{O}_3$  by  $(\text{NaPO}_3)_6$ .

$\Delta$ Turbidity first remains at about 100–400 NTU, then it reaches a turning point and then sharply increases until it gradually saturates. When the total  $\text{Na}^+$  concentration exceeds the turning point, the  $\text{Al}_2\text{O}_3$  suspension becomes unstable, and an apparent precipitate appears on the bottom of the beaker. Fig. 2(b) summarizes the turning points of the total  $\text{Na}^+$  concentration corresponding to different concentrations of  $\text{PO}_3^{2-}$ . As can be seen, the upper left unstable and bottom right stable zones are separated by the turning points. Moreover, as the  $\text{PO}_3^{2-}$  concentration increases, the turning point of the total  $\text{Na}^+$  concentration gradually increases.

Fig. 2(c) shows the effects of  $\text{PO}_3^{2-}$  and  $\text{Na}^+$  on the dispersion of  $\text{Al}_2\text{O}_3$ . For the mechanism,  $(\text{NaPO}_3)_6$  can be hydrolyzed in an aqueous solution to form long chain structures in which there are a lot of negatively charged  $\text{PO}_3^{2-}$ .  $\text{PO}_3^{2-}$  can be adsorbed on the  $\text{Al}_2\text{O}_3$  surface probably through hydrogen bonding.<sup>17,18</sup> On the one hand, the zeta potential of  $\text{Al}_2\text{O}_3$  becomes more negative due to the adsorbed negatively charged  $\text{PO}_3^{2-}$ . On the other hand, the steric hindrance between  $\text{Al}_2\text{O}_3$  increases due to the long-chain structure of the adsorption layer.<sup>16</sup> Therefore, the stability of  $\text{Al}_2\text{O}_3$  is improved. As for  $\text{Na}^+$ , it can enter the electric double layer of  $\text{Al}_2\text{O}_3$ , neutralizing the zeta potential and compressing the electric double layer. Consequently, the stability of  $\text{Al}_2\text{O}_3$  is weakened.

In summary,  $\text{PO}_3^{2-}$  and  $\text{Na}^+$  play opposite roles in dispersing  $\text{Al}_2\text{O}_3$ . For a certain concentration of  $\text{PO}_3^{2-}$ , the total  $\text{Na}^+$  concentration should be lower than the turning point to attain high stability when preparing an  $\text{Al}_2\text{O}_3$ -containing slurry.

### 3.2 CMP performance of $\text{Al}_2\text{O}_3$ -containing slurries

Based on the above stability results, 5 mM  $(\text{NaPO}_3)_6$  was chosen to disperse 1 wt%  $\text{Al}_2\text{O}_3$  powder in ultrapure water to prepare an  $\text{Al}_2\text{O}_3$  suspension. Fig. 3(a) shows the stability results. After standing for 24 h, the  $\text{Al}_2\text{O}_3$  suspension at the natural pH value is quite stable without any apparent precipitate on the bottom of the beaker. The average particle size is 142 nm.

On this basis, a tantalum CMP slurry containing ultrapure water, 1 wt%  $\text{Al}_2\text{O}_3$  powder, 5 mM  $(\text{NaPO}_3)_6$ , 0.4 wt%  $\text{H}_2\text{O}_2$  and

10 mM NaOH was prepared. The stability was examined at different pH values. Fig. 3(b) shows the stability results. After standing for 24 h, the  $\text{Al}_2\text{O}_3$ -containing slurries at pH 2 to 10 are all very stable and can be used for the following CMP.

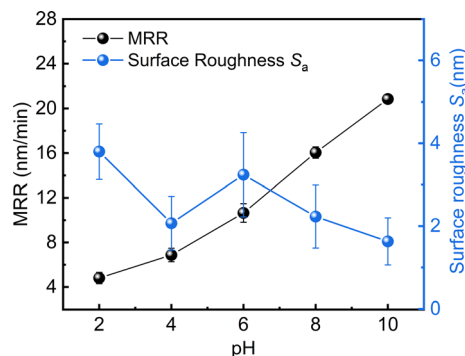


Fig. 4 MRR and surface roughness  $S_a$  results after polishing with the  $\text{Al}_2\text{O}_3$ -containing slurries at different pH values.

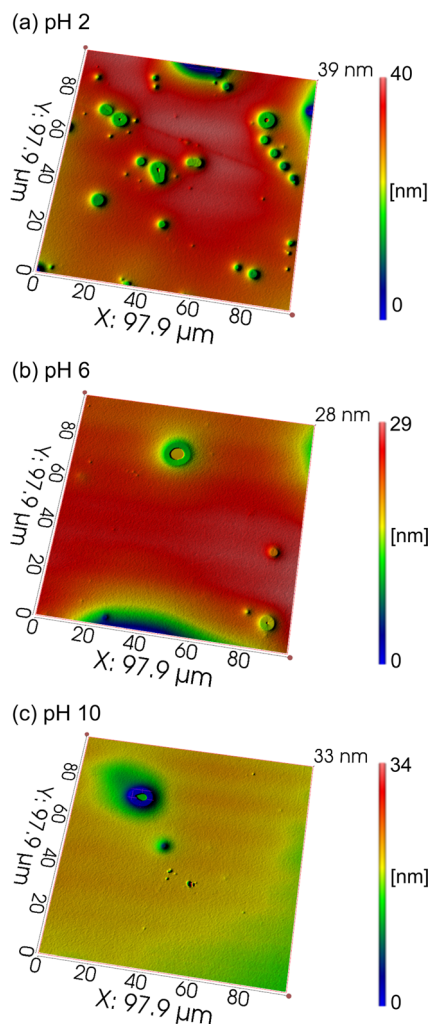


Fig. 5 Corresponding topographies of tantalum after polishing with the  $\text{Al}_2\text{O}_3$ -containing slurries at different pH values. (a) pH 2. (b) pH 6. (c) pH 10.

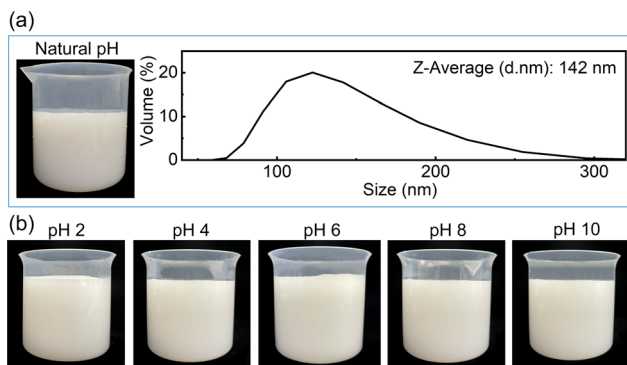


Fig. 3 Stability results of the  $\text{Al}_2\text{O}_3$  suspension and slurries with 5 mM  $(\text{NaPO}_3)_6$  as the dispersant. (a) The  $\text{Al}_2\text{O}_3$  suspension at the natural pH after standing for 24 h. The particle size distribution was measured by Zetasizer Nano (Malvern Instruments Ltd.). (b) The  $\text{Al}_2\text{O}_3$ -containing slurries at pH 2 to 10 after standing for 24 h.



Fig. 4 shows the MRR and surface roughness  $S_a$  results of tantalum after polishing with the above stable slurries at different pH values. With the increase in the pH value, the MRR gradually increases. The MRR reaches the maximum value at pH 10. Overall, the surface roughness  $S_a$  first decreases and then tends to be stable. The surface roughness  $S_a$  reaches 1.6 nm at pH 10.

Fig. 5 shows the corresponding topographies of tantalum after polishing. At pH 2, the topography is quite rough with many surface defects. In comparison, at pH 10, the topography becomes much smoother, and the surface defects are largely reduced.

To conclude, at pH 10, a relatively high MRR and satisfactory surface quality of tantalum can be obtained. Therefore, alkaline

pH is recommended for the  $\text{Al}_2\text{O}_3$ -containing CMP slurry for tantalum.

### 3.3 TEM and EDS characterization of $\text{Al}_2\text{O}_3$ before and after CMP

The above results reveal that  $\text{Al}_2\text{O}_3$  can be used as an effective abrasive for the tantalum CMP. To explore the role of  $\text{Al}_2\text{O}_3$  in the tantalum CMP, we used TEM and EDS to characterize  $\text{Al}_2\text{O}_3$  before and after polishing, aiming to investigate the interaction between  $\text{Al}_2\text{O}_3$  and the tantalum surface. Fig. 6 shows the TEM dark-field images and EDS results. As shown in Fig. 6(a), before polishing,  $\text{Al}_2\text{O}_3$  in the slurry contains Al, O, P and Na elements. Al is from  $\text{Al}_2\text{O}_3$ , O can be from  $\text{Al}_2\text{O}_3$  and  $(\text{NaPO}_3)_6$ , P is from  $(\text{NaPO}_3)_6$ , while Na can be from  $(\text{NaPO}_3)_6$  and NaOH. As shown

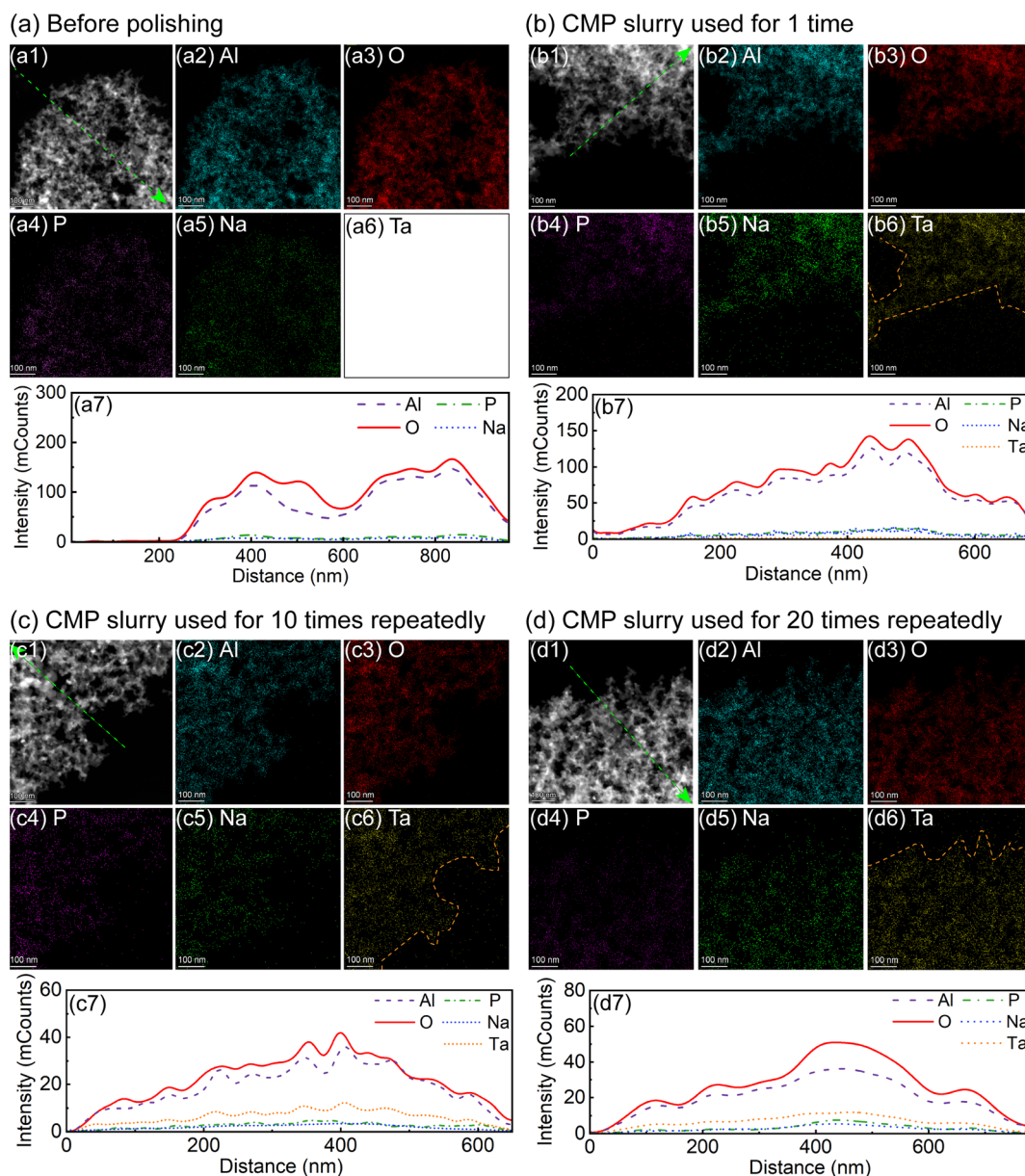


Fig. 6 TEM dark-field images and EDS results of  $\text{Al}_2\text{O}_3$  in the used slurries. (a) Before polishing. (b) After polishing with the CMP slurry used for 1 time. (c) After polishing with the CMP slurry used for 10 times repeatedly. (d) After polishing with the CMP slurry used for 20 times repeatedly.

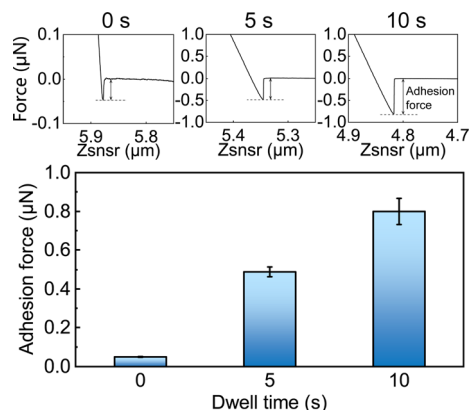


Fig. 7 The force–distance curves and the corresponding statistics of the adhesion force between the  $\text{Al}_2\text{O}_3$  microsphere tip and the tantalum surface in the solution containing ultrapure water, 0.4 wt%  $\text{H}_2\text{O}_2$ , 5 mM  $\text{Na}^+$ , and at pH 10. The applied load was fixed at 0.5  $\mu\text{N}$ . The dwell time was varied.

in Fig. 6(b) to (d), after polishing with the same CMP slurries 1 time, 10 times repeatedly, and 20 times repeatedly, the Ta element can be observed, and the distribution areas almost coincide with those of Al, O, P and Na. This suggests that Ta element can be adsorbed on the active sites of the  $\text{Al}_2\text{O}_3$  surface, which may be the reason for the excellent CMP performance of

the  $\text{Al}_2\text{O}_3$ -containing slurry at pH 10. In addition, the active sites may include hydroxyl group sites,  $\text{Al}^{3+}$  sites, and so on.<sup>19,20</sup>

### 3.4 AFM characterization of the interaction between $\text{Al}_2\text{O}_3$ and tantalum

The above TEM and EDS results indicate that Ta can be adsorbed on the  $\text{Al}_2\text{O}_3$  surface. We used AFM to explore the adsorption from the microscopic perspective. The adhesion force between the  $\text{Al}_2\text{O}_3$  microsphere tip and the tantalum surface in the solution was measured. The solution contained ultrapure water, 0.4 wt%  $\text{H}_2\text{O}_2$ , 5 mM  $\text{Na}^+$ , and at pH 10. Fig. 7 shows the variation trend of the adhesion force with the dwell time. Under an applied load of 0.5  $\mu\text{N}$ , the adhesion force gradually increases from 0.048 to 0.799  $\mu\text{N}$  as the dwell time increases from 0 to 10 s. In principle, the adhesion force can be affected by van der Waals force, electrostatic force, capillary force, and chemical interaction.<sup>21,22</sup> The capillary force can be neglected in the CMP slurry.<sup>23,24</sup> Under the fixed applied load, the van der Waals force and electrostatic force remain basically unchanged, suggesting that the increased adhesion force is mainly attributed to the enhanced chemical interaction. Additionally, according to the research of Li *et al.*<sup>25</sup> and Tian *et al.*,<sup>26</sup> the increased dwell time will lead to an increase in the number of chemical bonds formed, resulting in an enhancement of the interfacial interaction. Therefore, it can be concluded that

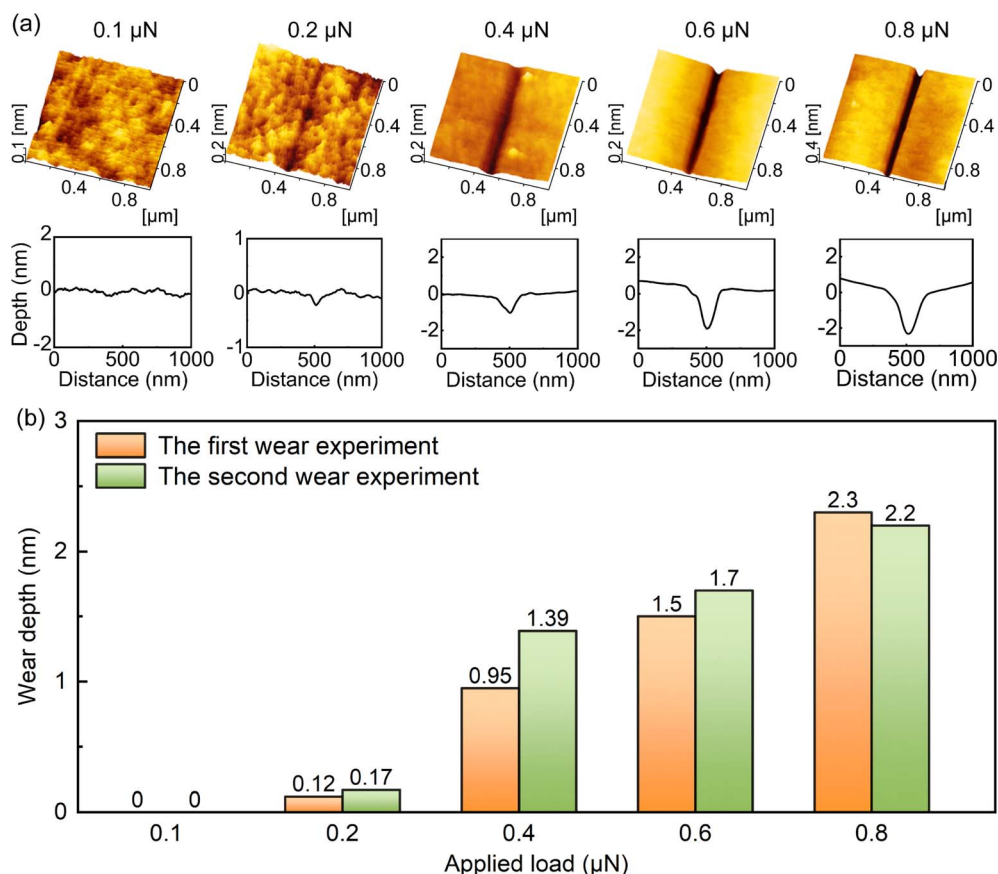


Fig. 8 Results of the AFM wear experiments under different applied loads in the solution containing ultrapure water, 0.4 wt%  $\text{H}_2\text{O}_2$ , 5 mM  $\text{Na}^+$ , and pH 10. (a) The topographies and average cross-section profiles of the wear areas. (b) The statistical results of the wear depth.



chemical interaction can exist between  $\text{Al}_2\text{O}_3$  and the tantalum surface, which can affect the material removal in the tantalum CMP. In the following study, we performed first-principles calculation to investigate the chemical interaction between  $\text{Al}_2\text{O}_3$  and the tantalum surface.

AFM wear experiments were performed to examine whether the chemical interaction between  $\text{Al}_2\text{O}_3$  and the tantalum surface can affect the material removal of tantalum. An  $\text{Al}_2\text{O}_3$  microsphere tip was rubbed against the tantalum surface in the solution, simulating the tantalum CMP. The solution contained ultrapure water, 0.4 wt%  $\text{H}_2\text{O}_2$ , 5 mM  $\text{Na}^+$ , and at pH 10. Fig. 8 shows the AFM wear results of tantalum. In particular, each condition was repeated twice to avoid excessive wear of the  $\text{Al}_2\text{O}_3$  microsphere tip, similar to the literature.<sup>27–29</sup> As shown in Fig. 8(a), no wear scar can be observed on the tantalum surface at 0.1  $\mu\text{N}$  applied load. In comparison, a shallow wear scar appears on the tantalum surface at 0.2  $\mu\text{N}$ . Moreover, as the applied load increases from 0.2  $\mu\text{N}$  to 0.8  $\mu\text{N}$ , the wear scar becomes deeper and clearer, and the wear depth gradually increases from about 0.1 nm to 2.3 nm (as shown in Fig. 8(b)).

Fig. 9 exhibits the  $\text{Al}_2\text{O}_3$  microsphere tip after the wear experiments. No apparent wear track can be observed on the

$\text{Al}_2\text{O}_3$  tip, and the profile is still spherical. The fitting radius of the  $\text{Al}_2\text{O}_3$  tip is about 3.116  $\mu\text{m}$ , which is close to the nominal value. In our case, Hertz contact theory was used to roughly estimate the contact pressure between the  $\text{Al}_2\text{O}_3$  tip and the tantalum surface. At 0.2  $\mu\text{N}$  applied load, the maximum contact pressure is calculated to be 0.48 GPa ( $P_{\text{max}} = (6F_{\text{applied}}E^*/\pi^3R^2)^{1/3}$ ). For calculation,  $F_{\text{applied}}$  is the applied load, that is 0.2  $\mu\text{N}$  here;  $E^* = [(1 - \nu_1^2)/E_1 + (1 - \nu_2^2)/E_2]^{-1}$ .<sup>30</sup> The Young's modulus  $E_1$  and Poisson ratio  $\nu_1$  of tantalum are 186 GPa and 0.35, respectively.<sup>31</sup> The Young's modulus  $E_2$  and Poisson ratio  $\nu_2$  of  $\text{Al}_2\text{O}_3$  are 370 GPa and 0.22, respectively;<sup>32</sup>  $R$  is the radius of the  $\text{Al}_2\text{O}_3$  microsphere tip).

Generally, yield strength is positively correlated with hardness.<sup>33</sup> As reported by Hariharaputhiran *et al.*,<sup>34</sup> the bulk hardness of the tantalum surface film is 1100–1200  $\text{kg mm}^{-2}$ , which is much larger than 230  $\text{kg mm}^{-2}$  of tantalum. Therefore, it can be inferred that the yield strength of the tantalum surface film should be higher than that of tantalum. As shown in Fig. 8(a), a shallow wear scar appears on the tantalum surface at 0.2  $\mu\text{N}$ . Combined with the calculation result based on Hertz contact theory, the material removal of tantalum starts at a contact pressure of 0.48 GPa, which is much lower than the yield strength of tantalum (about 6–19 GPa (ref. 35 and 36)), let alone that of the tantalum surface film.

To conclude,  $\text{Al}_2\text{O}_3$  can remove tantalum in the slurry under a contact pressure much lower than the yield strength of the tantalum surface film, which is quite similar to the material removal of silicon.<sup>37</sup> A reasonable explanation can be that when  $\text{Al}_2\text{O}_3$  slides on the tantalum surface, tribochemical reactions occur, lowering the energy barrier for dissociation of the interfacial bond and/or the subsurface back bond.<sup>38</sup>

### 3.5 First-principles calculation of interaction between $\text{Al}_2\text{O}_3$ and tantalum

In this section, we performed first-principles calculations based on DFT to further explore the interaction between  $\text{Al}_2\text{O}_3$  and the tantalum surface. As reported, tantalum can be oxidized to  $\text{Ta}_2\text{O}_5$  in the  $\text{H}_2\text{O}_2$ -containing slurry at alkaline pH.<sup>5,39</sup> Therefore, the interaction between  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  was investigated. Fig. 10(a) exhibits the models of  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$  and the  $\text{Al}_2\text{O}_3$ /

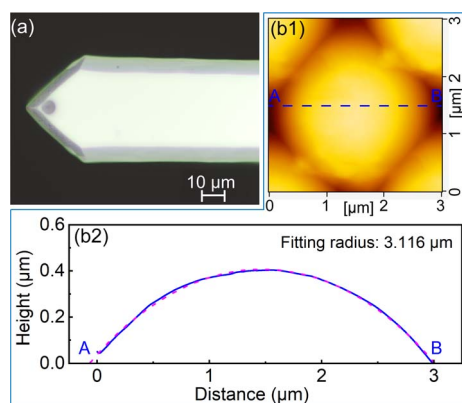


Fig. 9  $\text{Al}_2\text{O}_3$  microsphere tip after the AFM wear experiments. (a) The optical image of the  $\text{Al}_2\text{O}_3$  tip. It was measured with an optical microscope (Axio Lab.A1, ZEISS). (b1) The AFM inverse image of the  $\text{Al}_2\text{O}_3$  tip. (b2) The cross-sectional profile of the  $\text{Al}_2\text{O}_3$  tip along A–B in (b1). The dashed line in (b2) is the fitting curve.

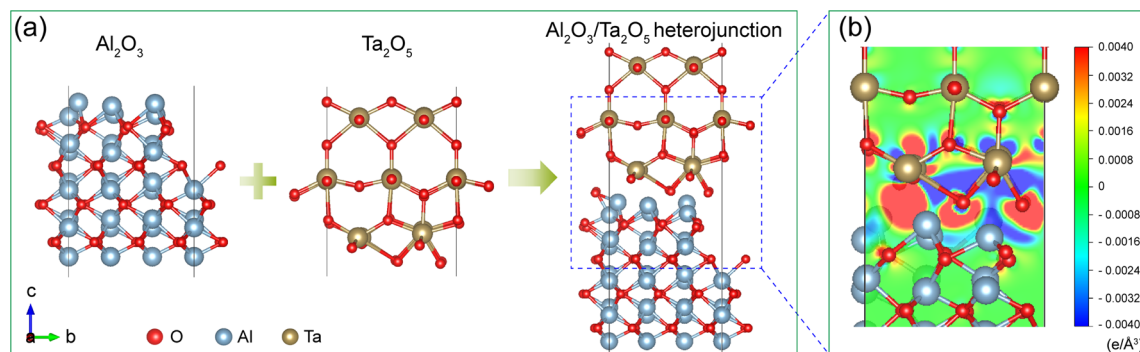


Fig. 10 Establishment of the  $\text{Al}_2\text{O}_3$ / $\text{Ta}_2\text{O}_5$  heterojunction model and calculation of the charge density difference. (a) The  $\text{Al}_2\text{O}_3$ / $\text{Ta}_2\text{O}_5$  heterojunction model. (b) The charge density difference of the  $\text{Al}_2\text{O}_3$ / $\text{Ta}_2\text{O}_5$  heterojunction at the interface.





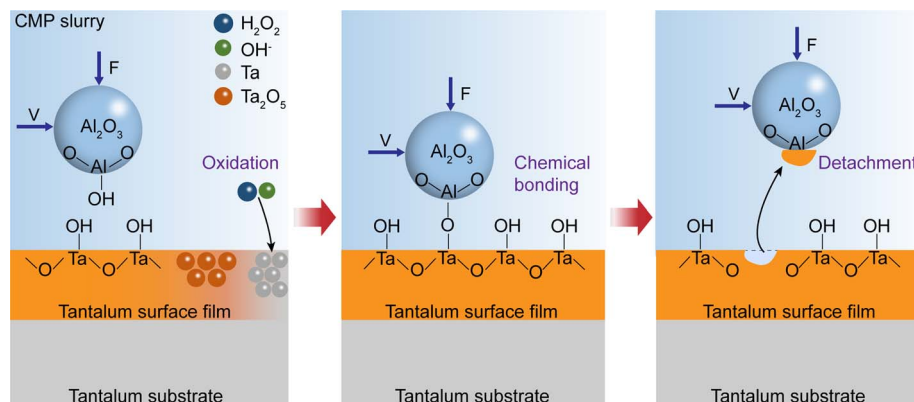


Fig. 11 Schematic diagram of the role of  $\text{Al}_2\text{O}_3$  abrasive in the tantalum CMP.

$\text{Ta}_2\text{O}_5$  heterojunction. The binding energy of the  $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$  heterojunction can be calculated as follows:

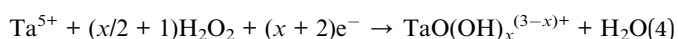
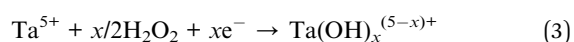
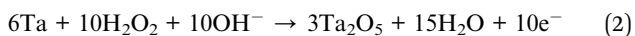
$$E = E_{\text{Al}_2\text{O}_3} + E_{\text{Ta}_2\text{O}_5} - E_{\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5} \quad (1)$$

$E_{\text{Al}_2\text{O}_3}$ ,  $E_{\text{Ta}_2\text{O}_5}$ ,  $E_{\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5}$  are the energies of  $\text{Al}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ , and the  $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$  heterojunction, which are calculated to be  $-438.52$  eV,  $-400.92$  eV, and  $-863.46$  eV, respectively.<sup>40</sup> By simple calculation, the binding energy of the  $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$  heterojunction is  $24.02$  eV, indicating a strong interaction existing between  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ .<sup>41</sup>

Moreover, the charge density difference of the  $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$  heterojunction is obtained by subtracting the isolated bottom ( $\text{Al}_2\text{O}_3$ ) and upper ( $\text{Ta}_2\text{O}_5$ ) surfaces from the total interface (the  $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$  heterojunction). As shown in Fig. 10(b), the red and blue areas indicate enrichment and depletion of the electron due to the interaction between  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$ , respectively. The  $\text{Al}_2\text{O}_3$  side is surrounded by red areas, while the  $\text{Ta}_2\text{O}_5$  side is surrounded by blue areas, suggesting that electrons transfer from  $\text{Ta}_2\text{O}_5$  to  $\text{Al}_2\text{O}_3$ , and form a chemical bond of  $\text{Al}-\text{O}-\text{Ta}$  at the  $\text{Al}_2\text{O}_3/\text{Ta}_2\text{O}_5$  interface, which may weaken the  $\text{Ta}-\text{O}$  back bond and facilitate the removal of Ta atoms to some extent.<sup>42</sup>

### 3.6 Role of $\text{Al}_2\text{O}_3$ abrasive in tantalum CMP

Based on the results obtained so far and the literature, the role of  $\text{Al}_2\text{O}_3$  abrasive in the tantalum CMP can be proposed. Fig. 11 demonstrates the corresponding schematic diagram. In the  $\text{H}_2\text{O}_2$ -containing slurry at alkaline pH, tantalum can be oxidized to form an oxide layer on the surface, which is mainly composed of  $\text{Ta}_2\text{O}_5$  and  $\text{Ta}-\text{OH}$  complexes with hydroxyl groups. The chemical reactions can be depicted as follows:<sup>39,43</sup>



Moreover,  $\text{Al}_2\text{O}_3$  can also be hydrolyzed to form hydroxyl groups.<sup>7</sup>

When  $\text{Al}_2\text{O}_3$  presses and slides on the tantalum surface, similar to silicon,<sup>38,44</sup> tribochemical reactions can occur.

Hydroxyl groups on the two contact surfaces are close to each other, and a dehydration reaction may occur to form the chemical bond of  $\text{Al}-\text{O}-\text{Ta}$  at the interface (partly confirmed by the above first-principles calculation).<sup>45,46</sup> As  $\text{Al}_2\text{O}_3$  moves, the interfacial chemical bond is stretched, and tantalum is detached from the tantalum surface. Eventually, the material removal of tantalum is achieved. In particular, as revealed by the AFM wear experimental results, the threshold contact pressure is much lower than the yield strength of the tantalum surface film when tantalum is removed, implying that the formation and stretching of the chemical bond of  $\text{Al}-\text{O}-\text{Ta}$  may lower the energy barrier for the dissociation of the  $\text{Ta}-\text{Ta}$  bond and/or  $\text{Ta}-\text{O}$  bond (weakening of the  $\text{Ta}-\text{O}$  back bond is confirmed by the above first-principles calculation).<sup>37</sup>

In addition, Li *et al.*<sup>6</sup> and Hariharaputhiran *et al.*<sup>34</sup> used  $\text{Al}_2\text{O}_3$  (the mean aggregate size is 290–360 nm, Ferro Electronics) to polish tantalum. The MRR decreases with the increase in the hardness of the softening layer on the tantalum surface. Therefore, it can be concluded that  $\text{Al}_2\text{O}_3$  may have a mechanical effect. Likewise,  $\text{Al}_2\text{O}_3$  in this study may also mechanically abrade the tantalum surface besides chemical bonding. More investigation is ongoing.

This study suggests that chemical interaction exists between  $\text{Al}_2\text{O}_3$  and the tantalum surface, helping achieve the material removal of tantalum. Therefore, to further enhance the CMP efficiency of tantalum, it is recommended to continuously increase the active sites that bind tantalum on the  $\text{Al}_2\text{O}_3$  surface, for example hydroxyl groups.<sup>47</sup>

## 4 Conclusions

This study investigated the interaction mechanism of  $\text{Al}_2\text{O}_3$  abrasive in the tantalum CMP using CMP and several characterization techniques including TEM, EDS, AFM, and first-principles calculation. Based on the results obtained so far, the conclusions can be drawn as follows:

(1)  $(\text{NaPO}_3)_6$  can be used as an effective dispersant for  $\text{Al}_2\text{O}_3$  powder in water.  $\text{PO}_3^-$  can improve the stability of  $\text{Al}_2\text{O}_3$  through electrostatic repulsion and steric hindrance, while  $\text{Na}^+$  deteriorates it. The total  $\text{Na}^+$  concentration should be lower than the turning point to attain a highly stable  $\text{Al}_2\text{O}_3$





suspension. For the tantalum CMP, with stable  $\text{Al}_2\text{O}_3$ -containing slurries, a relatively high MRR and satisfactory surface quality of tantalum can be obtained at pH 10.

(2) TEM and EDS characterization results indicate that Ta element can be absorbed on the  $\text{Al}_2\text{O}_3$  surface, which can be attributed to the chemical interaction between  $\text{Al}_2\text{O}_3$  and the tantalum surface (confirmed by AFM adhesion force measurement), forming the chemical bond of Al–O–Ta (partly confirmed by first-principles calculation). Moreover, AFM wear experimental results show that the  $\text{Al}_2\text{O}_3$  microsphere tip can remove tantalum under 0.48 GPa, which is much lower than the yield strength of the tantalum surface film.

(3) For the CMP mechanism, with  $\text{H}_2\text{O}_2$  and at alkaline pH, tantalum can be oxidized to  $\text{Ta}_2\text{O}_5$  and Ta–OH complexes, and  $\text{Al}_2\text{O}_3$  can be hydrolyzed. When  $\text{Al}_2\text{O}_3$  presses and slides on the tantalum surface, tribochemical reactions can occur. Hydroxyl groups on the two contact surfaces may be dehydrated to form the chemical bond of Al–O–Ta at the interface. As  $\text{Al}_2\text{O}_3$  moves, the interfacial chemical bond is stretched, and tantalum is detached. Eventually, the material removal of tantalum is achieved.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of interest

There are no conflicts of interest to declare.

## Acknowledgements

This work is supported by the National Natural Science Foundation of China (51991373, and 52235004), the National Key R&D Program of China (2020YFA0711001), and the Fundamental Research Funds for the Central Universities (2682024CG007).

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