

## Article

# Effect of Polyoxyethylene-Based Nonionic Surfactants on Chemical–Mechanical Polishing Performance of Monocrystalline Silicon Wafers

Bowen Jiang, Jie Guan, Peng Zhao, Yulin Chen and Zefang Zhang \*

Research Center for Advanced Micro-/Nano- Fabrication Materials, College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, China; m340121120@sues.edu.cn (B.J.)

\* Correspondence: zefangzhang@163.com

**Abstract:** The use of surfactants is crucial in the chemical–mechanical polishing fluid system for silicon wafers. This paper examines the impact of the functional group structure of polyoxyethylene-based nonionic surfactants and the variation in the polyoxyethylene (EO) addition number on the polishing performance of monocrystalline silicon wafers, to achieve the appropriate material removal rate and surface quality. The results demonstrated that the straight-chain structure of fatty alcohol polyoxyethylene ether (AEO-9) exhibited superior performance in wafer polishing compared to octylphenol polyoxyethylene ether (OP-9) and isoprenol polyoxyethylene ether (TPEG) and polyethylene glycol (PEG). By varying the number of EO additions of AEO-type surfactants, this study demonstrated that the polishing performance of monocrystalline silicon wafers was affected by the number of EO additions. The best polishing effect was achieved when the number of EO additions was nine. The mechanism of the role of polyoxyethylene-type nonionic surfactants in silicon wafer polishing was derived through polishing experiments, the contact angle, abrasive particle size analysis, zeta potential measurement, XPS, and other means of characterization.



**Citation:** Jiang, B.; Guan, J.; Zhao, P.; Chen, Y.; Zhang, Z. Effect of Polyoxyethylene-Based Nonionic Surfactants on Chemical–Mechanical Polishing Performance of Monocrystalline Silicon Wafers. *Crystals* **2024**, *14*, 460. <https://doi.org/10.3390/crust14050460>

Academic Editors: Giancarlo Salviati and Vladimir Chigrinov

Received: 2 April 2024

Revised: 7 May 2024

Accepted: 10 May 2024

Published: 14 May 2024



**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Keywords:** monocrystalline silicon wafer; chemical–mechanical polishing; polyoxyethylene-based nonionic surfactant; structure; polishing mechanism

## 1. Introduction

The semiconductor industry is rapidly developing, leading to increasingly high performance and precision requirements for devices. Despite the emergence of third- and fourth-generation semiconductors, over 90% of current semiconductor devices and integrated circuits still use silicon wafers as the substrate material [1–3]. In semiconductor process engineering, chemical–mechanical polishing is the only technology recognized for achieving the global flattening of the wafer surface [4–7]. The process of polishing monocrystalline silicon wafers involves three main stages: rough polishing, medium polishing, and fine polishing. Rough polishing could increase the removal rate to quickly eliminate the damaged layer on the surface of silicon wafers. Intermediate polishing further removes surface damage and reduces surface roughness. Fine polishing is intended to completely remove the damaged layer on the surface, control surface micro-defects, and obtain a smooth and clean surface for subsequent processing [8]. Surfactants are a crucial component of the polishing solution in the chemical–mechanical polishing (CMP) process [9–13].

Nonionic surfactants were widely researched and applied due to their ability to mix well with other types of surfactants. They are difficult to strongly adsorb on solid surfaces, easy-to-clean, and stable with good compatibility. Xu et al. [14] discovered that nonionic surfactant fatty alcohol polyoxyethylene ether (AEO) could form a protective layer on the surface of Cu wafers and abrasive grains, improving the surface quality of the wafers after polishing. Similarly, Yang et al. [15] observed the strong surface activity of two

additives, AEO-9 and O-20, during the silicon wafer polishing process. Qu et al. [16] discovered that the use of surfactants in the polishing solution aided in the elimination of abrasive particles from the surface of the wafer. Song et al. [17] discovered that the nonionic surfactant polyethylene glycol improves the surface quality of wafers after polishing in wafer polishing. Zhao et al. [18] demonstrated that cationic surfactants polyvinyl amide and AEO can inhibit the flocculation of abrasive grains and reduce scratches on the wafer surface during the adsorption of silica sol abrasive grains. Zhang et al. [19] discovered that the inclusion of FA/O nonionic surfactants could considerably decrease the surface roughness of the wafer after CMP polishing. Song et al. [20] researched the use of surfactants in the post-CMP cleaning of Cu and found that the addition of nonionic surfactant AEO-9 can enhance the cleaning effect.

Previous research has demonstrated the significance of surfactants in the polishing of silicon wafers. However, the impact of polyoxyethylene-type nonionic surfactant structures on silicon wafer polishing is less studied. In this study, the role of six different surfactants was investigated, four of which were polyoxyethylene-type nonionic surfactants with different functional group structures, and the other two were AEO surfactants with different EO additions. The pH of the polishing solution exerts a significant influence on the performance and characterization outcomes of wafer polishing. In this paper, a pH of 10.5 was selected as the base condition, based on previous findings and the literature [21,22]. It was demonstrated that the addition of surfactants employed in this study does not affect the pH of the polishing solution. The effect of the surfactants on both the polishing solution and the surface of silicon wafers was determined by polishing experiments, contact angle measurements, electrochemical tests, particle size measurements, surface characterization, X-ray photoelectron spectroscopy (XPS), friction and wear experiments, and zeta potential measurements.

## 2. Materials and Methods

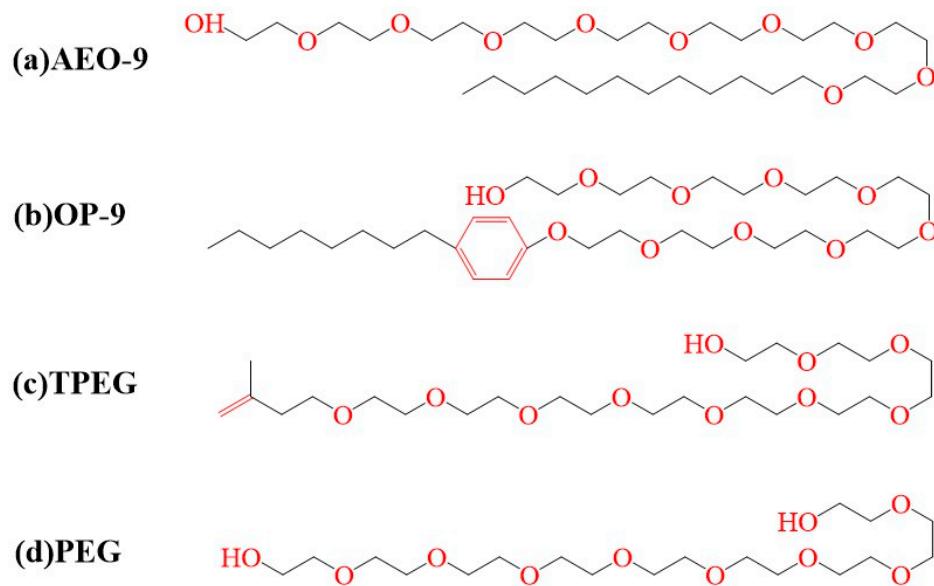
### 2.1. Chemical and Materials

Colloidal silicon dioxide (average diameter ~40 nm, 40% aqueous suspension, Shanghai Yingzhi Grinding Corp, Shanghai China) was used as an abrasive for CMP polishing experiments on monocrystalline silicon wafers. The wafers used were four-inch monocrystalline silicon wafers provided by Suzhou DeliYuan Electronic Technology Co. (Suzhou, China). They had a thickness of approximately 700  $\mu\text{m}$ , were N-type doped, crystalline <111>, and had a TTV of  $\leq 5 \mu\text{m}$  and a Warp of  $\leq 30 \mu\text{m}$ . Tetramethylammonium hydroxide (TMAH) from Shanghai McLean Biochemical Technology Co., Ltd. (Shanghai China) was used as the pH adjuster. The surfactants used were fatty alcohol polyoxyethylene ether (AEO-7, AEO-9, AEO-25; 99%), octylphenol polyoxyethylene ether (OP-9; 99%), polyethylene glycol (PEG; 99%), and isopentenyl alcohol polyoxyethylene ether (TPEG; 99%), all supplied by Shandong Yusuo Chemical Technology Co. (Heze, China). Figure 1 displays the molecular structures of AEO-9, OP-9, and TPEG.

All of the commonly used surfactants contain one or more functional groups. AEO-9 has a high ether bond (-C-O-C-) and a hydroxyl group (-OH) as well as a long carbon chain. OP-9 has a high ether bond (-C-O-C-) and a hydroxyl group (-OH) as well as a benzene ring. TPEG has a high ether bond (-C-O-C-) and a hydroxyl group (-OH) as well as a double bond. PEG has only a high ether bond (-C-O-C-) and hydroxyl group (-OH).

### 2.2. Preparation of CMP Slurry

The commercial silica sol was diluted with deionized water to reduce the  $\text{SiO}_2$  concentration to 0.3%. Next, 0.003% of the surfactant was added, followed by adjusting the pH to 10.5 using tetramethylammonium hydroxide (TMAH). Then, the usable polishing solution was obtained.



**Figure 1.** Chemical structures of various surfactants applied in this research, including (a) AEO-9, (b) OP-9, (c) TPEG, and (d) PEG.

### 2.3. CMP Experiments

The polishing experiments of monocrystalline silicon wafers were conducted using Polyurethane polishing pads (SUBA600, Shenzhen Fangda Grinding Technology Co., Ltd., Shenzhen, China) on a desktop polishing machine (SG0031 portable polishing machine, Shenzhen Weikanghua Machinery Co., Ltd., Shenzhen, China). Before CMP, the silicon wafer surface was cleaned with 0.1% hydrofluoric acid to remove the oxide layer. The primary polishing parameters are listed in Table 1. Each experiment set in the CMP trials was repeated three times to ensure result accuracy.

**Table 1.** Si CMP process parameters.

Process Parameters	Value
Polishing time	20 min
Pad rotation speed	45 rpm
Wafer rotation speed	40 rpm
Slurry feed rate	200 mL/min
Pressure	2 psi

After polishing, the wafer surface was thoroughly cleaned with deionized water. The thickness of the wafer was measured before and after polishing using a thickness profilometer (Shanghai Starner Electronic Technology Co., Ltd., Shanghai, China). The wafer's material removal rate (MRR, nm/min) was calculated by subtracting the thickness after polishing from the thickness before polishing (five-point scale), using the following Equation (1):

$$\text{MRR} = \frac{\Delta H}{t} \quad (1)$$

where  $\Delta H$  (nm) is the averaged thickness difference between the pre- and post-polished films at 5 different locations, and  $t$  is the polishing time ( $t = 20$  min). MRR is the average of three individual polishing tests.

### 2.4. Characterization

The quality of the surface of single-crystal silicon wafers after polishing was analyzed using an atomic force microscope (Nanosurf Isostage 300, Nasser Nanotechnology Co., Ltd., Beijing, China) with a scanning range of  $10\ \mu\text{m} \times 10\ \mu\text{m}$  and an accuracy of 0.01 nm.

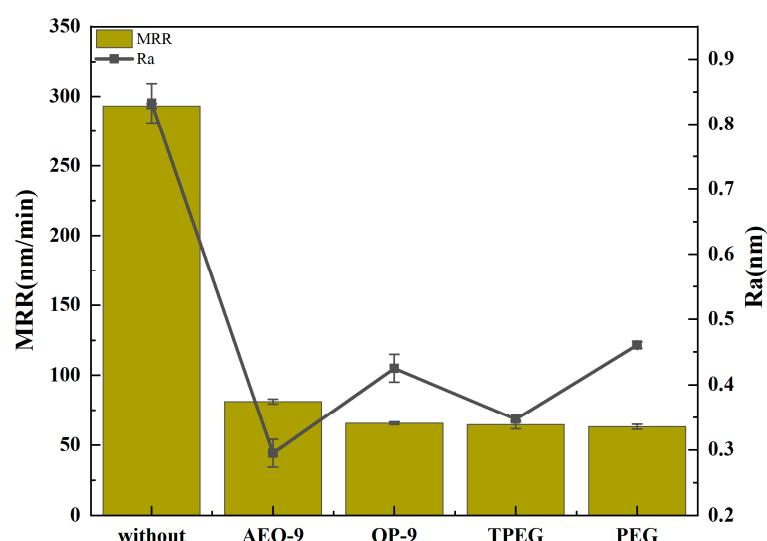
Additionally, the contact angle was measured using a contact angle measuring instrument (SDC-200S, Dongguan Shengding Precision Instrument Co., Ltd., Dongguan, China). The particle size of silica in the polishing solution and the zeta potential were measured using a Malvern nanoparticle size meter (Zetasizer Nano ZS90, Shanghai Spectrum Instrument Systems Co., Ltd., Shanghai, China). The Tafel curves for single-crystal silicon wafers were derived in different AEO surfactant polishing solutions using the CHI660E electrochemical workstation. The coefficient of friction of the polishing fluid on the surface of silicon wafers was measured using a multifunctional vertical friction and wear tester (MVF-1A, Jinan Hengxu Testing Machine Technology Co., Ltd., Jinan, China). The surface chemical analysis of silicon wafers was measured using a ray photoelectron spectrometer (Thermo Scientific K-Alpha, Waltham, MA, USA). The elemental species and content of Si, O, C, and N on the surface of the Si wafer were also measured.

### 3. Results

#### 3.1. The Effect of Surfactants with Different Functional Groups on the Polishing Performance of Monocrystalline Silicon Wafers

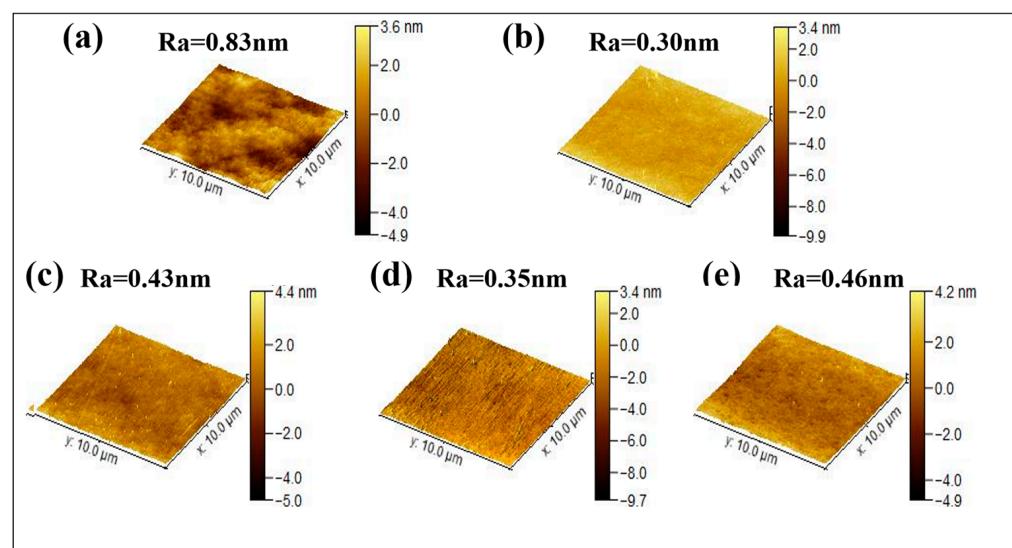
To examine the impact of four surfactants on the polishing rate of monocrystalline silicon wafers, CMP experiments were conducted on the polishing solution with the addition of the four surfactants.

Figure 2 illustrates a comparison of the polishing rate of monocrystalline silicon wafers with and without the various surfactants in a polishing solution system with a pH of 10.5. Comparing the wafers, the MRR values were observed to follow the descending order of AEO-9 > TPEG > OP-9 > PEG, while the Ra values followed the descending order of PEG > OP-9 > TPEG > AEO-9. It is noteworthy that the addition of AEO-9 to the wafers resulted in the highest MRR value and the smallest Ra value. It has been demonstrated that the adsorption efficiency of different surfactants declines with the elongation of the carbon chain of the hydrophobic group and the augmentation of the number of hydroxyl groups of the hydrophilic group at a constant concentration [23]. AEO-9 and OP-9 have similar hydrophilic terminal groups to TPEG and PEG, suggesting that the observed differences in properties may be related to the structure of the hydrophobic terminal groups. In comparison to PEG with only hydrophilic groups, the wafer polishing properties are influenced by the change in the hydrophobic end of the surfactant. It can be observed that -C-O-C- binding to the straight carbon chain is more effective than -C-O-C- binding to the benzene ring and to -C-O-C- binding to the double bond.



**Figure 2.** Effect of surfactants with different functional groups on MRR and Ra of monocrystalline silicon wafers.

Figure 3 displays the 3D morphology of the Si surface under different surfactant conditions. The addition of a surfactant resulted in a better surface than the case of no surfactant, with the best surface morphology observed when AEO-9 was added. The figure illustrates that surfactants can effectively improve the defects on the wafer surface. Specifically, the addition of AEO-9 reduces the surface roughness of wafers by over 60%. In addition to its molecular structure, the activity of a surfactant is also dependent on its hydrophilic-lipophilic balance (HLB) value [24]. In terms of HLB values, PEG > TPEG > OP-9 > AEO-9. Studies have shown that the lower the HLB value, the greater the likelihood of micelle formation and the higher the surface tension [24,25]. The polishing performance of monocrystalline silicon wafers was affected differently by these. This was not only due to the chemical composition of the polishing solution system but also to the changes in the particle size of the abrasive grains and the wettability of the wafer surface. To study the polishing mechanism of three different surfactants on single-crystal silicon wafers, it is necessary to investigate the effects of abrasive particle size and changes in contact angle on the wafer surface.

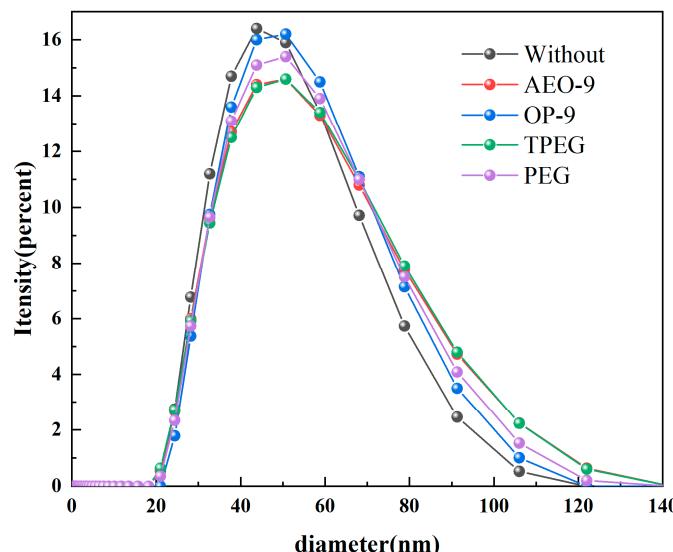


**Figure 3.** The surface morphology of silicon wafers after polishing (a) without surfactants, (b) with AEO-9, (c) with OP-9, (d) with TPEG, and (e) with PEG.

The addition of surfactants to the polishing solution resulted in alterations to the grain size of the abrasive grains. This, in turn, affected the material removal rate and surface roughness of the wafers. It was demonstrated that these changes were linked to the adsorption of surfactant molecules on the surface of the abrasive grains [26]. The hydroxyl (-OH) structure in the molecule of polyoxyethylene nonionic surfactants could form Si···O-H-type hydrogen bonds with colloidal  $\text{SiO}_2$ , thus forming monolayer adsorption on the surface of  $\text{SiO}_2$  particles. Furthermore, changes in the surfactant molecular structure could affect the particle size and particle size distribution of colloidal  $\text{SiO}_2$ . Table 2 illustrates the impact of various surfactants on the particle size of colloidal silica. Overall, the addition of surfactants resulted in an increase in the average particle size of the  $\text{SiO}_2$  abrasive grains compared to the case without surfactants. By combining the silica particle size distributions presented in Figure 4, it was evident that surfactant molecules were adsorbed onto the silica surface. The adsorption effect of AEO-9 and TPEG is more pronounced than that of OP-9 and PEG.

**Table 2.** Changes in the mean particle size and polydispersity index of SiO<sub>2</sub> were observed in the presence of various surfactants.

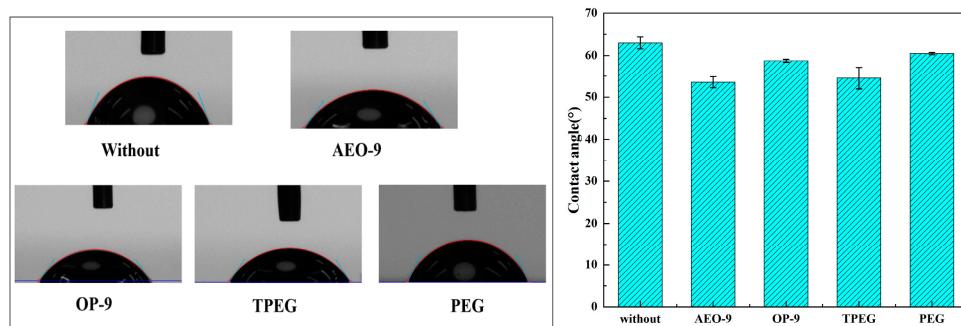
Various Surfactants	Mean Particle Sizes/nm	Polydispersity Index
Without	45.35	0.095
AEO-9	46.08	0.102
OP-9	45.91	0.1
TPEG	46.23	0.115
PEG	46.26	0.083



**Figure 4.** SiO<sub>2</sub> particle size distribution changes due to various surfactants.

The contact angle was a crucial indicator of the liquid's wettability on the solid surface [27]. To elucidate the impact of three surfactants with distinct structures on the surface quality of silicon wafers after CMP, we measured the contact angle of polishing liquids containing these surfactants on the surface of single-crystal silicon wafers. Figure 5 shows that surfactants reduced the contact angle of the polishing solution on the wafer surface (Use different colors lines to show the size of the contact angle). The contact angle was measured at 63° without the addition of surfactant. With the addition of AEO-9, OP-9, TPEG, and PEG, the contact angle decreased to 53.55°, 58.75°, 54.55°, and 60.5°, respectively. Compared to the other two surfactants, AEO-9 resulted in a lower contact angle. This was beneficial for bonding between the polishing solution and the wafer surface, as well as energy transfer. These changes coincided with the alterations in the MRR and Ra values of the monocrystalline silicon wafers after polishing.

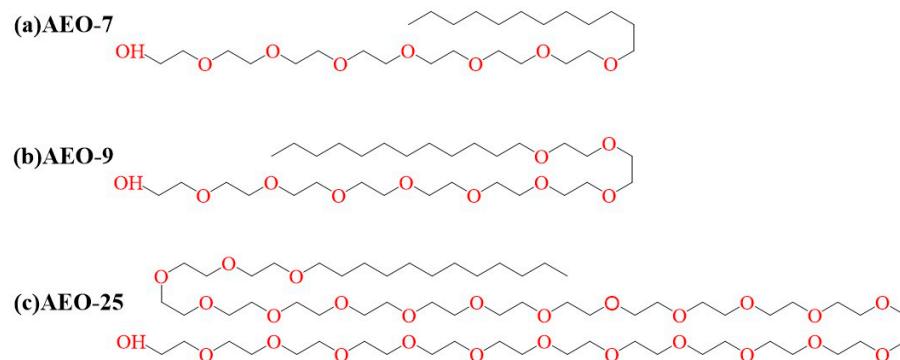
The surface quality of wafers can be effectively improved by adding polyoxyethylene-type surfactants to the monocrystalline silicon wafer polishing liquid system. By comparing the effects of four different structural functional groups of polyoxyethylene-based surfactants on the polishing performance of monocrystalline silicon wafers, it was found that surfactants with a hydrophobic group structure were superior to those with only a polyoxyethylene-based structure, and that the combination of -C-O-C- with a straight carbon chain was superior to the combination of -C-O-C- with a benzene ring or double bond. Contact angle and abrasive grain size measurements were used to determine the effect of surfactant molecules on wafer surface wetting and adsorption on the abrasive grain surface. To discuss the effect of the surfactant structure on wafer polishing performance, we investigate the impact of AEO surfactants with different EO addition numbers below.



**Figure 5.** Variation in surface contact angle of single-crystal silicon under different surfactant conditions.

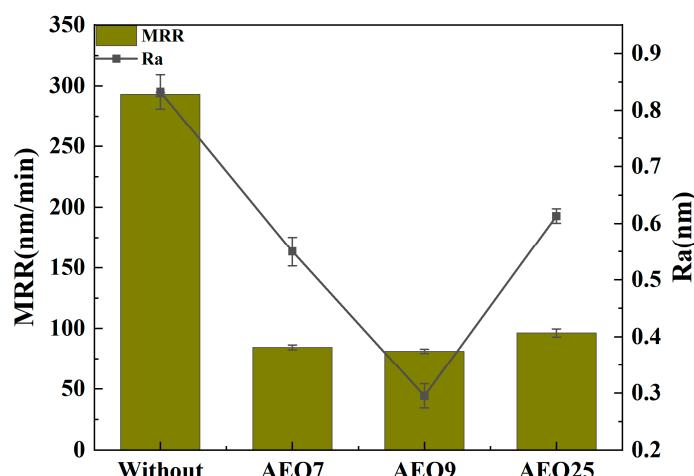
### 3.2. The Effect of AEO Surfactants with Varying EO Addition Numbers on the Polishing Performance of Monocrystalline Silicon Wafers

To examine the impact of various EO addition numbers at the hydrophilic end of the active agent on the polishing performance of monocrystalline silicon wafers, three fatty alcohol polyoxyethylene ethers with different EO addition numbers were chosen. Their structures are illustrated in Figure 6.



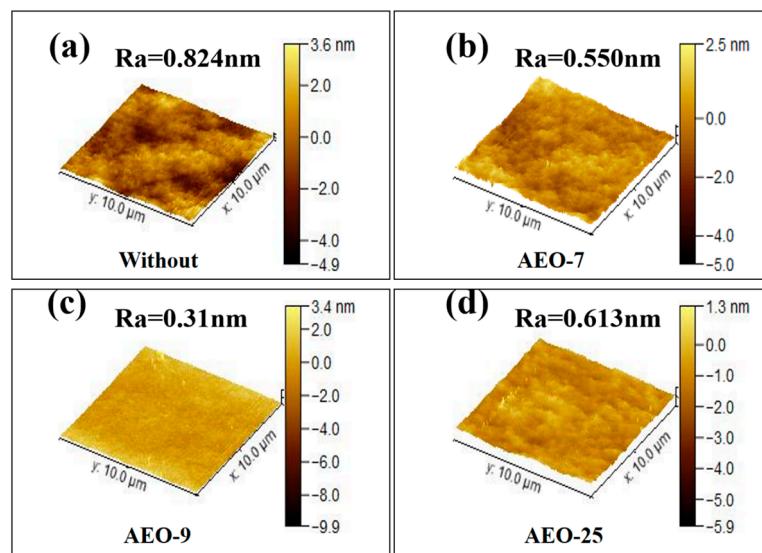
**Figure 6.** Molecular structures of AEO-7, AEO-9, and AEO-25.

The polishing rate of monocrystalline silicon wafers was investigated by examining the effect of AEO surfactants with varying EO addition numbers, as illustrated in Figure 7. The alteration of the AEO surfactant EO number resulted in a decrease followed by an increase in both the material removal rate and surface roughness of the silicon wafers.



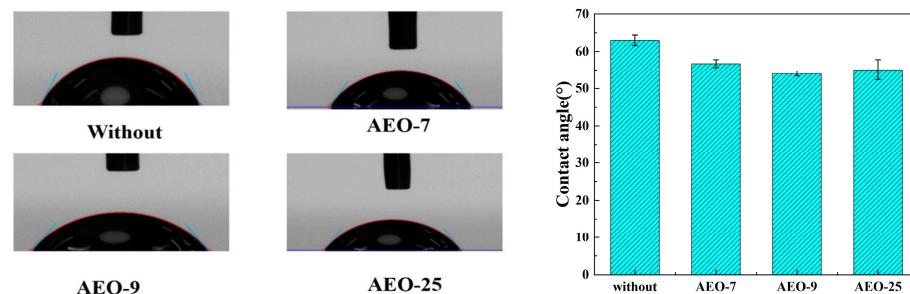
**Figure 7.** Effect of AEO surfactants with different EO additions on MRR and Ra of monocrystalline silicon wafers.

Figure 8 shows that the surface roughness initially decreased and then increased with an increase in the number of EO additions. The protective effect of fatty alcohol polyoxyethylene ether increased with the increase in polyoxyethylene groups due to its adsorption effect. This led to an increase in spatial potential resistance between abrasive grains and the surface of silicon wafers. However, when the polyoxyethylene chain was too long, it might fold and collide in the solution system and on the surface of silicon wafers. Therefore, the addition of AEO-25 improved the removal rate slightly compared to the remaining two actives, but it also reduced the surface quality after polishing.



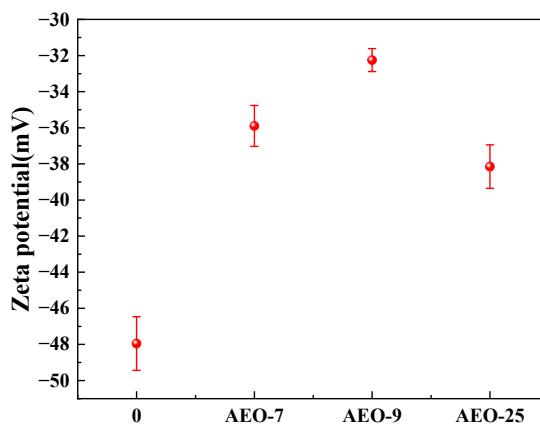
**Figure 8.** The surface morphology of silicon wafers after polishing (a) without surfactants, (b) with AEO-7, (c) with AEO-9, and (d) with AEO-25.

Figure 9 shows that the contact angle decreased as the number of AEO surfactant additions increased, but the contact angle increased when the EO addition number was 25 (Use different colors lines to show the size of the contact angle). This was because, at higher addition numbers, the active agent's tendency to adsorb on the  $\text{SiO}_2$  particles decreased due to the spatial site resistance effect, resulting in enhanced surface tension. The contact angle's magnitude depended primarily on the cohesion and adhesion within the system [28]. Cohesion refers to the force between molecules in a solution, while adhesion is the force exerted by the solid on the liquid. Surfactants can be added to the polishing solution to reduce cohesion between molecules and enhance adhesion. This improved the diffusion ability of the polishing solution on the wafer surface, reduced the contact angle, and improved the wetting ability of the wafer surface. High hydrophilicity can effectively prevent particle adsorption during the polishing process. Compared to other fatty alcohol polyoxyethylene ethers, AEO-9 exhibited superior wetting ability on the surface of monocrystalline silicon wafers.



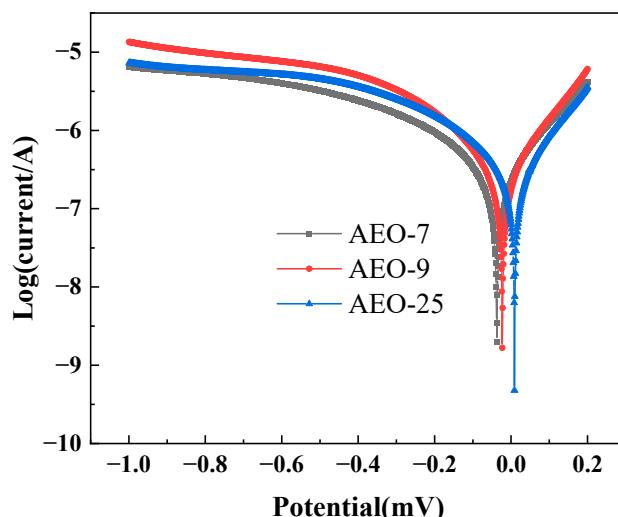
**Figure 9.** Variation of contact angle on single crystal silicon surface under the condition of AEO surfactants with different EO addition number.

Zeta potential is a measurement of the strength of mutual repulsion or attraction between particles. It is known that under alkaline conditions, silicon wafers and silica particles have the same charge, both negative. When the absolute zeta potential value is smaller, it can be inferred that the two have less repulsive force. The nanoscale adsorption layer of AEO surfactant on the colloidal silicon dioxide abrasive prevents the damage caused by the direct contact between the colloidal silicon dioxide abrasive and the surface of the silicon wafer, which improves the surface quality of the silicon wafer. It is commonly used to determine the stability of a colloid. A colloid is considered stable when the absolute value of the zeta potential is greater than 30 mV [29]. Figure 10 shows that the addition of the AEO-type surfactant did not affect the stability of the silica sol system. The system was not ionized in water and existed in the form of molecules. It formed a layer of hydration film around the silica sol, resulting in better spatial potential stability.



**Figure 10.** Variation in zeta potential of colloidal silica in polishing solution with different surfactants at pH 10.5.

Figure 11 and Table 3 illustrate that the corrosion potential gradually increased with the addition of the AEO-type surfactant EO. The corrosion current density decreased and then increased. AEO-9 had the lowest corrosion current density, indicating that the addition of the AEO surfactant formed a passivation film on the surface of the wafer. This attenuated the corrosion effect of the alkali on the surface of the wafer and weakened the erosive effect of the polishing solution, thus improving the surface quality of the polished wafer. The protective effect of AEO-9 was stronger than that of AEO-7 and AEO-25.

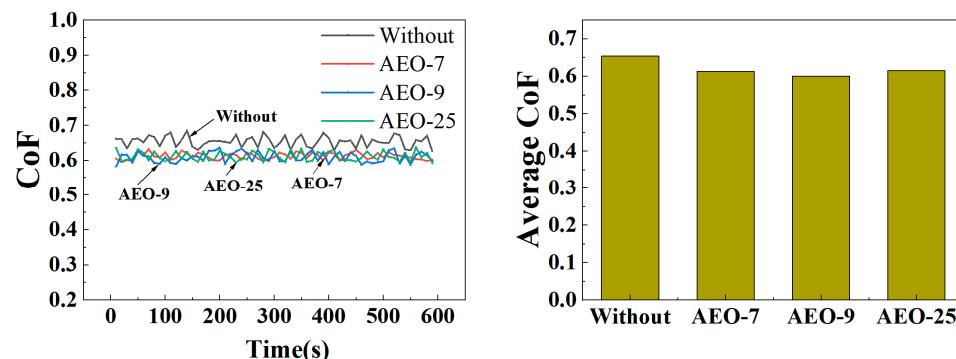


**Figure 11.** Changes in the polarization curves of different surfactants at pH 10.5 in the polishing solution at the kinetic point position.

**Table 3.** Corrosion potentials and corrosion current densities for Si in the polishing solution with different types of surfactants at pH 10.5.

Various Surfactants	Mean Ecorr (V)	Mean Log Icorr (A/cm <sup>2</sup> )
AEO-7	−0.0384	−6.7883
AEO-9	−0.0290	−6.8820
AEO-25	0.0112	−6.6968

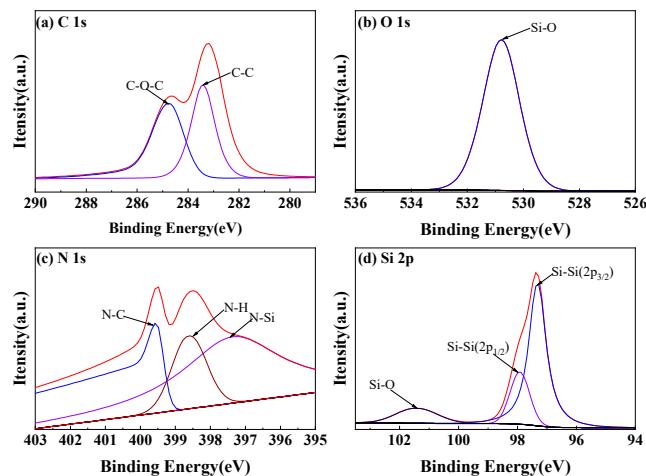
During the chemical mechanical polishing process, material removal occurred due to direct frictional wear between the polishing fluid, polishing pad, and wafer surface [30,31]. The amount of removed material was determined by the material's properties and the environment of the polishing fluid, as well as the direct friction between the polishing pad and the wafer. The coefficient of friction (COF) during the polishing process is measured through frictional wear experiments. This measurement was valuable for explaining the variation in the material removal rate, as well as for optimizing the polishing fluid's formulation. The component mechanism was also of great value. The measurement results are shown in Figure 12. The friction coefficient is 0.654 without the addition of the AEO surfactant. However, the friction coefficient decreased with the AEO surfactant. At the addition number of 9, the friction coefficient reached its lowest value of 0.6, which was lower than that of 7 and 25. This suggests that the lubrication ability between the polishing solution and the wafer is improved with the addition of the AEO surfactant, reducing the mechanical action between the abrasive particles and the surface of the wafer. Simultaneously, the surfactant creates a thin film on the wafer surface, safeguarding it from corrosion and enhancing the surface quality post-polishing. This aligned with the alteration in the wafer's material removal rate and surface quality.



**Figure 12.** The coefficient of friction (CoF) between the surface of a silicon wafer and fatty alcohol polyoxyethylene ethers with varying EO addition numbers.

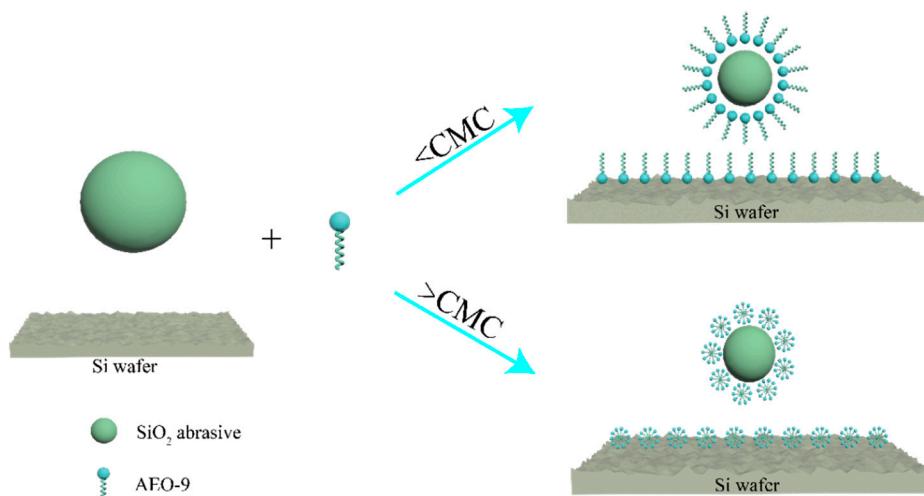
To investigate the adsorption of the polishing solution with the AEO surfactant on the wafer surface, we analyzed the composition of the wafer surface after polishing with the solution. Figure 13 displays the XPS spectra of C, O, N, and Si of monocrystalline silicon wafers after polishing. Figure 13a exhibits the C 1s spectra of the surface of single-crystal silicon wafers after polishing. The peaks at 285.8 eV and 284.1 eV were attributed to C-O-C and C-C [32,33], respectively, indicating the adsorption of fatty alcohol polyoxyethylene ether (AEO-9) containing ether bonds on the wafer surface during the polishing process. The binding energy at 532.4 eV was found to correspond to Si-O (Figure 13b) [34]. The peaks at 397.6 eV, 398.4 eV, and 399.8 eV corresponded to N-Si, N-H, and N-C (Figure 13c) [28]. The Si2p spectrum in Figure 13d exhibited binding energies at 99.72 eV and 99.10 eV, which corresponded to Si 2p(1/2) and Si 2p(3/2) of the Si-Si bond, respectively. The peak at 102.73 was attributed to the Si-O peak [21,28]. Upon analyzing each spectrum, it was evident that the fatty alcohol polyoxyethylene ether could be adsorbed onto the wafer's surface to create a protective film during the polishing process. The formed Si-O bond protected

the wafer's surface from the corrosive effects of the alkali, thereby achieving the desired protective effect.



**Figure 13.** The binding state of Si after polishing by slurries measured by XPS (a) C 1s, (b) O 1s, (c) N 1s, and (d) Si 2p.

A model of the mechanism of fatty alcohol polyoxyethylene ether in the polishing process of monocrystalline silicon wafers has been established, combined with the experimental results mentioned above. It was indicated that fatty alcohol polyoxyethylene ether played two primary roles in the polishing process. The first reason was due to the internal structure of the silica particles' nucleus, which was associated with the three-dimensional mesh structure of the Si-O-Si bond. Additionally, a Si-OH polar molecular bond was formed on the interface which was contacted with water. This was further enhanced by the polishing solution of fatty alcohol polyoxyethylene ether, which was adsorbed on the surface of silica abrasive grains. Due to the spatial resistance effect, the repulsive force between the particles was enhanced, preventing the agglomeration of particles. However, the hydrogen bonding effect caused the active agent molecules to adsorb onto the wafer's surface, creating a passivation film. This weakened the mechanical interaction between the particles and the wafer, resulting in a reduced removal rate of wafer material. As a result, the surface quality after polishing was improved. Based on the theory of surfactant micelles, micelles can be formed in a solution system when the amount of surfactant exceeds the critical micellar concentration (CMC) [35], as illustrated in Figure 14.



**Figure 14.** The mechanism of the addition of fatty alcohol polyoxyethylene ether to the surface of  $\text{SiO}_2$  abrasive particles and silicon wafers.

#### 4. Conclusions

This study aimed to examine the impact of polyoxyethylene-based nonionic surfactants on the polishing performance of monocrystalline silicon wafers by altering their functional group structure and EO addition number and to explore their mechanism of action. Based on the results obtained, the following conclusions can be drawn:

- (1) The surface quality of wafers can be effectively improved by adding polyoxyethylene-type surfactants to the monocrystalline silicon wafer polishing liquid system. A combination of a hydrophobic structure and a polyoxyethylene structure was found to be more effective than a surfactant with only a polyoxyethylene structure. Furthermore, a surfactant with a straight carbon chain was found to be more effective than a surfactant with a benzene ring or double bond.
- (2) It was discovered that altering the EO number of the AEO surfactant affects the wafer polishing performance. The surface quality of the polished wafers improves initially but then deteriorates with an increase in the EO addition number.
- (3) The mechanism of the polyoxyethylene-type surfactant in the silicon wafer polishing process was speculated through a series of characterization methods. Surfactant molecules can adsorb on both the  $\text{SiO}_2$  abrasive grains and the silicon wafer surface. Adsorption on the  $\text{SiO}_2$  abrasive grains can weaken the mechanical interaction between the abrasive grains and the wafer surface. Simultaneously, the active agent molecules formed a layer of passivation film on the surface of the silicon wafer, to inhibit corrosion. Additionally, the surfactants enhance the wetting and dispersing properties, resulting in the increased energy exchange between the polishing solution and the silicon wafer surface. This led to an improvement in the surface quality of the wafer after polishing.

**Author Contributions:** B.J. designed the experiment project. J.G. proposed the analysis of the effective theoretical model. B.J. performed the experiment results. Y.C. wrote the manuscript and sent it to all authors. P.Z., J.G. and Y.C. revised the paper and suggested some advice. Z.Z. promoted the funding support. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was funded by the National Natural Science Foundation of China; the grant number was 52075318, and the one of funder was Zefang Zhang.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The datasets used and analyzed during the current study are available from the corresponding author upon reasonable request.

**Acknowledgments:** We also thank Shanghai Yingzhi Grinding Corp for providing colloidal silica samples used in this study.

**Conflicts of Interest:** The authors declare no conflicts of interest.

#### References

1. Xiao, C.; Deng, C.; Zhang, P.; Qian, L.; Kim, S.H. Interplay between solution chemistry and mechanical activation in friction-induced material removal of silicon surface in aqueous solution. *Tribol. Int.* **2020**, *148*, 106319. [[CrossRef](#)]
2. Xiao, C.; Chen, C.; Wang, H.; Chen, L.; Jiang, L.; Yu, B.; Qian, L. Effect of counter-surface chemistry on defect-free material removal of monocrystalline silicon. *Wear* **2019**, *426*, 1233–1239. [[CrossRef](#)]
3. Hochberg, M.; Harris, N.C.; Ding, R.; Zhang, Y.; Novack, A.; Xuan, Z.; Baehr-Jones, T. Silicon photonics: The next fabless semiconductor industry. *IEEE Solid-State Circuits Mag.* **2013**, *5*, 48–58. [[CrossRef](#)]
4. Wang, Y.G.; Zhang, L.C.; Biddut, A. Chemical effect on the material removal rate in the CMP of silicon wafers. *Wear* **2011**, *270*, 312–316. [[CrossRef](#)]
5. Chen, P.H.; Huang, B.W.; Shih, H.-C. A chemical kinetics model to explain the abrasive size effect on chemical mechanical polishing. *Thin Solid Film.* **2005**, *476*, 130–136. [[CrossRef](#)]
6. Lei, H.; Zhang, P. Preparation of alumina/silica core-shell abrasives and their CMP behavior. *Appl. Surf. Sci.* **2007**, *253*, 8754–8761. [[CrossRef](#)]

7. Zhang, P.; Chen, G.; Ni, Z.; Wang, Y.; Teng, K.; Qian, S.; Bian, D.; Zhao, Y. The effect of Cu<sup>2+</sup> ions and glycine complex on chemical mechanical polishing (CMP) performance of SiC substrates. *Tribol. Lett.* **2021**, *69*, 94. [[CrossRef](#)]
8. Hong, J.; Niu, X.; Wang, J.; Wang, C.; Zhang, B.; Wang, R.; Sun, M.; Liu, Y. Research on Si (100) crystal substrate CMP based on FA/O alkaline slurry. *Appl. Surf. Sci.* **2017**, *420*, 483–488. [[CrossRef](#)]
9. Lee, J.-D.; Park, Y.-R.; Yoon, B.U.; Han, Y.-P.; Hah, S.; Moon, J.-T. Effects of nonionic surfactants on oxide-to-polysilicon selectivity during chemical mechanical polishing. *J. Electrochem. Soc.* **2002**, *149*, G477. [[CrossRef](#)]
10. Jiang, L.; He, Y.; Niu, X.; Li, Y.; Luo, J. Synergetic effect of benzotriazole and non-ionic surfactant on copper chemical mechanical polishing in KIO<sub>4</sub>-based slurries. *Thin Solid Film.* **2014**, *558*, 272–278. [[CrossRef](#)]
11. Neirynck, J.M.; Yang, G.-R.; Murarka, S.P.; Gutmann, R.J. The addition of surfactant to slurry for polymer CMP: Effects on polymer surface, removal rate and underlying Cu. *Thin Solid Film.* **1996**, *290*, 447–452. [[CrossRef](#)]
12. Asghar, K.; Qasim, M.; Nelabhotla, D.M.; Das, D. Effect of surfactant and electrolyte on surface modification of c-plane GaN substrate using chemical mechanical planarization (CMP) process. *Colloids Surf. A Physicochem. Eng. Asp.* **2016**, *497*, 133–145. [[CrossRef](#)]
13. Tsai, T.-H.; Wu, Y.-F. Effects of nonionic surfactants on performance of copper chemical mechanical polishing. *Chem. Eng. Commun.* **2006**, *193*, 702–714. [[CrossRef](#)]
14. Xu, Q.; Chen, L.; Yang, F.; Cao, H. Influence of slurry components on copper CMP performance in alkaline slurry. *Microelectron. Eng.* **2017**, *183*, 1–11. [[CrossRef](#)]
15. Yang, X.; Fang, Q.; Sun, M.; Qi, M. Experimental and Theoretical Study on the Influence of Fatty Alcohol Polyoxyethylene Ether on the Surface Roughness of Silicon in Alkaline Solutions. *ECS J. Solid State Sci. Technol.* **2024**, *13*, 014002. [[CrossRef](#)]
16. Qu, L.; Gao, B.; Wang, X.; Wu, T.; Tan, B. Effect of intermolecular interaction of compound surfactant on particle removal in post-Cu CMP cleaning. *ECS J. Solid State Sci. Technol.* **2021**, *10*, 064007. [[CrossRef](#)]
17. Enmin, S.; Da, B.; Hao, X. Effect of guanidine carbonate and polyethylene glycol on CMP of single crystal silicon wafer. *Res. Prog. SSE* **2022**, *42*, 63–67.
18. Zhao, Q.; Xie, S.; Wang, H.; Yang, L.; Mei, X.; He, Y. Control of the Micro-defects on the surface of silicon wafer in chemical mechanical polishing. *ECS J. Solid State Sci. Technol.* **2022**, *11*, 023009. [[CrossRef](#)]
19. Zhang, Y.; Niu, X.; Zhou, J.; Yang, C.; Hou, Z.; Zhu, Y. Effect of FA/O II surfactant as a complex non-ionic surfactant on copper CMP. In Proceedings of the 2021 China Semiconductor Technology International Conference (CSTIC), Shanghai, China, 14–15 March 2021; pp. 1–3.
20. Song, G.; Tan, B.; Liu, Y.; Wang, C. Role of AEO-9 as nonionic surfactant in Barrier Slurry for Copper Interconnection CMP. In Proceedings of the 2020 China Semiconductor Technology International Conference (CSTIC), Shanghai, China, 26 June–17 July 2020; pp. 1–3.
21. Li, J.; Liu, Y.; Dai, Y.; Yue, D.; Lu, X.; Luo, J. Achievement of a near-perfect smooth silicon surface. *Sci. China Technol. Sci.* **2013**, *56*, 2847–2853. [[CrossRef](#)]
22. Bae, J.-Y.; Han, M.-H.; Lee, S.-J.; Kim, E.-S.; Lee, K.; Lee, G.-s.; Park, J.-H.; Park, J.-G. Silicon wafer CMP slurry using a hydrolysis reaction accelerator with an amine functional group remarkably enhances polishing rate. *Nanomaterials* **2022**, *12*, 3893. [[CrossRef](#)]
23. Zhang, Q.; Li, Y.; Song, Y.; Li, J.; Wang, Z. Properties of branched alcohol polyoxyethylene ether carboxylates. *J. Mol. Liq.* **2018**, *258*, 34–39. [[CrossRef](#)]
24. Wang, X.; Wang, C.; Zhu, M.; Zhou, J.; Luo, C.; Chen, Z.; Yang, X.; Wang, H.; Zhang, X. Insight on Surface Changes Post Chemical Mechanical Polishing (CMP) of the Silicon Substrate by Adding Polyoxyethylene Ether. *ECS J. Solid State Sci. Technol.* **2023**, *12*, 114005. [[CrossRef](#)]
25. Matsaridou, I.; Barmpalexis, P.; Salis, A.; Nikolakakis, I. The influence of surfactant HLB and oil/surfactant ratio on the formation and properties of self-emulsifying pellets and microemulsion reconstitution. *AAPS PharmSciTech* **2012**, *13*, 1319–1330. [[CrossRef](#)] [[PubMed](#)]
26. Zhang, L.; Wang, S.; Wang, T.; Lu, X. Polishing mechanisms of various surfactants in chemical mechanical polishing relevant to cobalt interconnects. *Int. J. Adv. Manuf. Technol.* **2023**, *128*, 5425–5436. [[CrossRef](#)]
27. Liu, L.; Su, H.; Xing, J.; Peng, D.; Zhang, Q.; Qian, J. Corrosion inhibition and friction-reduction property of tetrazole derivatives on copper. *Anti-Corros. Methods Mater.* **2018**, *65*, 361–367. [[CrossRef](#)]
28. Hwang, H.-S.; Lim, J.-H.; Park, J.-H.; Choi, E.-S.; Ahn, J.-W.; Park, J.-G. Effect of hydroxyethyl cellulose concentration on surface qualities of silicon wafer after touch polishing process. *Electrochim. Solid-State Lett.* **2010**, *13*, H147. [[CrossRef](#)]
29. Zhou, J.; Niu, X.; Wang, Z.; Cui, Y.; Wang, J.; Yang, C.; Huo, Z.; Wang, R. Roles and mechanism analysis of chitosan as a green additive in low-tech node copper film chemical mechanical polishing. *Colloids Surf. A Physicochem. Eng. Asp.* **2020**, *586*, 124293. [[CrossRef](#)]
30. Suratwala, T.I.; Feit, M.D.; Steele, W.A. Toward deterministic material removal and surface figure during fused silica pad polishing. *J. Am. Ceram. Soc.* **2010**, *93*, 1326–1340. [[CrossRef](#)]
31. Li, Z.; Ina, K.; Lefevre, P.; Koshiyama, I.; Philipossian, A. Determining the effects of slurry surfactant, abrasive size, and abrasive content on the tribology and kinetics of copper CMP. *J. Electrochem. Soc.* **2005**, *152*, G299. [[CrossRef](#)]
32. Liu, J.; Jiang, L.; Wu, H.; Zhong, X.; Qian, L. Performance of carboxyl groups in chemical mechanical polishing of GCr15 bearing steel: Effects of carbon chain length and pH. *Tribol. Lett.* **2021**, *69*, 161. [[CrossRef](#)]

33. Zhou, J.; Niu, X.; Cui, Y.; Wang, Z.; Wang, J.; Wang, R. Study on the film forming mechanism, corrosion inhibition effect and synergistic action of two different inhibitors on copper surface chemical mechanical polishing for GLSI. *Appl. Surf. Sci.* **2020**, *505*, 144507. [[CrossRef](#)]
34. Zhang, X.; Wang, C.; Zhou, J.; Liu, Z.; Liu, G.; Ma, H.; Li, Y. Effect and mechanism of dual-official group of ethanolamines on the chemical mechanical polishing of monocrystalline silicon. *ECS J. Solid State Sci. Technol.* **2022**, *11*, 093005. [[CrossRef](#)]
35. Pratt, L.R.; Owenson, B.; Sun, Z. Molecular theory of surfactant micelles in aqueous solution. *Adv. Colloid Interface Sci.* **1986**, *26*, 69–97. [[CrossRef](#)]

**Disclaimer/Publisher’s Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.