Topical Review

Polishing and planarization of single crystal diamonds: state-of-the-art and perspectives

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Abstract
Diamond is a promising material for the modern industry. It is widely used in different applications, such as cutting tools, optical windows, heat dissipation, and semiconductors. However, these application areas require exceptionally flattened and polished diamond surfaces. Unfortunately, due to the extreme hardness and chemical inertness of diamond, the polishing of diamond is challenging. Since the 1920s, various conventional and modern mechanical, chemical, and thermal polishing techniques have been proposed and developed for finishing diamond surfaces. Therefore, to impart proper guidance on selecting a good polishing technique for production practice, this paper presents an in-depth and informative literature survey of the current research and engineering developments regarding diamond polishing. At first, a brief review of the general developments and basic material removal principles is discussed. This review concludes with a detailed analysis of each techniques’ polishing performance and critical challenges, and a discussion of the new insights and future applications of diamond polishing.

Keywords: diamond polishing, material removal anisotropy, ultra-smooth surface, chemical reaction, surface quality

1. Introduction
Diamond has some of the most extreme physical, optical, and mechanical properties of any material, such as the lowest friction coefficient, lowest compressibility, highest bulk modulus and thermal conductivity, broad optical transparency from deep ultraviolet (UV) to far-infrared, and extreme mechanical hardness and wear resistance, etc [1–3]. Diamonds have been used extensively in modern industrial applications, such as cutting tools, optical windows, and heat dissipation, etc [4]. The diamond crystals with a bandgap of 5.5 eV, electric field breakdown strength of 10 MV cm⁻¹, and high thermal conductivity of 2000 W MK⁻¹ are considered an ideal material for manufacturing high-performance semiconductor electronic components [5, 6]. In short, diamond is the most promising material for the modern industry of the 21st century.
Natural diamonds are mostly used for jewelry. From a technical viewpoint, the irregular shape and small size of natural diamond make it a difficult material to apply in optical windows and heat dissipation. Besides, the chemical vapor deposition (CVD), which developed rapidly over the last few decades [7–10], addressed the restrictions of the small quantity and size of traditional natural diamond and realized the low cost and mass production of synthetic diamonds. As a result, CVD ultimately facilitated the extensive application of diamonds in the optic, acoustic, thermal management, and semiconductor fields. Irrespective of the naturally excavated or artificially produced diamond crystal, industrial applications of diamond require high precision flattening to obtain ultra-smooth and damage-free surfaces. Moreover, the characteristic high hardness, wear resistance, high chemical inertness, and anisotropy makes machining diamonds extremely difficult. Therefore, the principles, processes, and types of equipment related to the ultra-precision polishing technology of diamond crystals have been a significant focus for both the academic and industrial communities.

Many polishing techniques have been developed to reduce the surface roughness of diamond crystal. The most frequently used methods include mechanical polishing (MP) [11–13], thermochemical polishing (TCP) [7, 14, 15], chemical-mechanical polishing (CMP) [8, 16], dynamic friction polishing (DFP) [17–19], laser polishing (LP) [20–22], ion beam polishing (IBP) [23–25], and hydroxyl (OH) radicals enhanced chemical polishing [26–29]. Each of the above techniques have unique beneficial characteristics, such as high material removal capabilities, the ability to obtain high quality polished surfaces, and low processing costs. Simultaneously, the selection of the polishing technique depends on the practical application and the dimensions of the pre-polished diamond. For instance, a moderate polishing technique should be chosen for application in ultra-thin wear-resistant or chemical-resistant diamond coatings. The situation is somewhat different for diamonds that are used in optical windows, requiring highly polished surfaces. Particularly, for thermal spreader applications, both sides of the diamond must be polished. It should be noted that broad applications of CVD diamond films have also introduced new challenges to current diamond polishing methods. This is because of the rough initial surface, large diameter, and thinness of CVD-produced diamonds, which brings an unprecedented inequity between efficiency and quality. Therefore, it is imperative to select a proper polishing technique that suits the domains of the desired applications and economic constraints.

This review aims to compile informative literature, research, and engineering developments about diamond polishing. To the best of the author’s knowledge, this paper is one of a kind as it provides a brief review of the history of diamond polishing, discussion on the basic material removal mechanisms, polishing performance and challenges faced by each technique, and future guidance to achieve new insights into the understanding of promising diamond polishing techniques for advanced future engineering applications.

2. A short chronological review of diamond polishing

2.1 General development of diamond polishing

The polishing of diamond jewels has a long history in human society. The first record of diamond polishing dates back to the mid 14th century [30]. European aristocrats chased diamonds as a symbol of power and wealth due to the jewels’ scarcity and beauty. As a result, diamond polishing has been historically reserved for jewelry needs and remained a trade secret controlled by a few jeweler families for centuries. The quantitative and systematic study of diamond grinding and polishing was first introduced by Tolkowsky et al in 1920 [30, 31]. Although this common diamond polishing method was highly effective, it had a low material removal rate (MRR). After decades of development, this method was summarized as MP, which is widely used in the commercial jewelry industry [4]. In the mid 20th century, Grodziniski [7] proposed a diamond polishing method assisted by a hot-metal-plate, which is now referred to as TCP. Yoshikawa et al [32] and Weima et al [15, 33] further investigated this new technique. Reports of diamond polishing peaked around the end of the 20th century.

In 1961, Evans et al [34] reported a diamond etching process at ambient conditions. This process was later termed reactive ion etching (RIE) [35, 36]. In this technique, various plasma ions can be generated from different reactive gases to polish diamond surfaces [37–39]. About 10 years later, in 1972, Spencer et al [40] reported his work on diamond milling by argon-ion beams, which was believed to be the beginning of diamond polishing by ion beam sputtering (IBS). Subsequently, both the RIE and IBS were summarized as IBP. In the same year, Thornton and Wilks et al [30] used thermal oxidation chemicals to improve the material removal efficiency and surface quality of MP, which emerged as a new technique called CMP. This method was further developed by Malshe et al [41, 42] and Kuhnle and Weis [43] to obtain an ultra-smooth diamond surface. Rothschild et al [44] proposed the LP of diamond in 1986, which was rapidly developed over the following decades [22, 45]. DPF developed by Kiyoshi Suzuki and his colleagues in the mid 1990s, is a relatively new diamond polishing technology [46], which was further improved by Chen and Zhang in the coming years [17, 23, 47–53]. The exploration of new methods of diamond polishing came to a suspension period after the 1990s. Since then, research on diamond polishing has mainly focused on combining and optimizing previously developed polishing methods.

The OH radical enhanced chemical polishing has attracted tremendous attention in recent years. The possibility of using OH radicals to oxidize and flatten a diamond surface was first confirmed by Tokuda et al in 2009 [26] and later improved by Kubota et al [27, 54, 55]. Combining OH radicals produced from an H₂O₂ solution with traditional MP can efficiently remove material diamond surfaces. In 2013, Watanabe et al [29] proposed an UV irradiation-assisted diamond polishing process, which utilized UV-induced photochemical reactions to produce active species, such as OH radicals and oxygen. Yamamura et al [28] developed a plasma-assisted polishing
(PAP) method that allows for damage-free diamond surface processing. The plasma discharge produces a large number of OH radicals that activate the rotating polishing plate surface. Material removal occurs when the activated polishing plate comes in contact with diamond surface. Hence, OH radicals is a common factor in these techniques that play an important role in removing materials from diamond surfaces. According to the reported studies, this newly developed method is a promising addition to existing diamond polishing technologies.

To describe a historical perspective of the field, a chronological presentation of the publications related to diamond polishing is shown in figure 1. A brief discussion of the developments during different periods is given as follows:

2.1.1. Stage 1: early studies (1920s–1970s). The systematic scientific research on diamond polishing during the 1920s–1960s mainly focused on improving diamond processing efficiency and optimizing processing parameters to satisfy the rapidly growing demands for jewelry. The traditional ‘Scaife’ polishing method, which was later named MP, was developed and has been widely used since then. It should be noted that the phenomenon of material removal anisotropy during MP was also observed and investigated. According to the results, the crystal orientation and sliding directions strongly influenced material removal efficiency and surface quality. The material removal anisotropy was addressed by exploring the TCP, which replaced the diamond grit coated cast-iron-plate with a hot-metal-plate. Unlike mechanical abrasion induced polishing, the material removal in TCP results from the thermo-chemical reaction between the hot metal plate and diamond surface. The preceding research highlights two dominant material removal mechanisms of diamond polishing, i.e., mechanical removal and chemical removal. Consequently, subsequent research primarily focuses on these two basic material removal mechanisms.

2.1.2. Stage 2: improved studies (1970s–2010s). Chemical removal proved to be a practical approach to overcome material removal anisotropy during diamond polishing. Thus, various chemical diamond polishing techniques were developed, such as CMP, DFP, LP, and IBP. These techniques were mainly driven by newly discovered physical and chemical phenomena. As a result, the study of material removal expanded dramatically. Different mechanisms such as oxidation reaction, tribo-chemistry reaction, graphitization, carbon solution, and RIE were investigated to understand material removal. Compared to traditional MP methods, the newly developed polishing techniques offer various advantages, such as higher MRR, better surface quality, and lower processing costs. Based on the discussion, it is not an exaggeration to claim that this period represents the passion years of optimizing and promoting diamond polishing techniques. During this period, the vast majority of current diamond polishing processes, such as mechanical, chemical, and physical, were tested individually or in various combinations.

2.1.3. Stage 3: recent state-of-art studies (2010s–2020s). A wide range of diamond applications in cutting tools, acoustics, and semiconductors require high material removal efficiency and surface roughness at the nanoscale and atomic-scale. These applications pose new challenges to existing polishing techniques. Unfortunately, not all of the developed polishing techniques meet the industrial requirements. Therefore, studies from the past decade have mainly focused on selective polishing techniques providing high processing efficiency and excellent surface quality. The development of molecular dynamics (MD) and quantum mechanics has promoted the analysis of atomic material removal mechanisms and improved the theoretical research regarding diamond polishing. Particularly, the rapid growth of visual simulation software allows for atomic evolution during diamond polishing, which promotes a deeper understanding of material removal mechanisms. Hence, stage 3 can be attributed to understanding the principle material removal mechanism of MP and the development of efficient and high-quality chemical-assisted polishing techniques.

2.2. The explored material removal mechanisms

Understanding the basic material removal mechanisms in diamond polishing is crucial when choosing the proper polishing method. In general, the material removal mechanisms can be divided into mechanical abrading and chemical reactions. However, the removal mechanisms should be further subdivided to better understand diamond polishing in reality. To the best of our knowledge, the material removal mechanisms employed in diamond polishing can be broadly classified as:

2.2.1. Micro-chipping. Tolkowsky et al conducted the first systematic research of material removal mechanisms and suggested that micro-chipping or micro-cleavage dominates material removal during the MP of diamonds. When a polishing plate moves relative to the diamond surface, the external mechanical pressure pushes the coated diamond grit into the diamond surface to wipe and remove carbon atoms from the substrate. It is believed that the frictional force between the diamond grit and substrate surface drives the brittle fracture process during the mechanical processing of diamonds, while material removal occurs once the frictional force is higher than the binding energy of the diamond atoms. Thus, a proportion of the diamond surface is easily chipped away when the applied frictional force exceeds the binding energy. The brittle fracture rate depends on the brittleness of processed material, the load applied on the grit, and the sliding speed of the grit relative to the substrate. However, the crystal orientation dependence of the binding energy in diamonds induces anisotropic material removal during MP. Therefore, it is useful to select a proper crystal orientation and sliding angle to obtain a high MRR when mechanically polishing diamonds.

2.2.2. Carbon diffusion. Carbon atoms are easily diffused into carbon-soluble metals, such as Fe, Ni, Mo, and rare-earth metals/alloys. This reaction can be triggered at the optimized
temperature and pressure during diamond polishing. When a diamond surface comes in contact with a metal plate, carbon atoms from the diamond surface diffuse into the metal until a saturation condition is achieved. The synergistic effect of the distinctive diffusion rates at the rough structures eventually flattens the diamond surface. The diffusion rate is determined by the distance from the polishing interface, the diffusion coefficient, and processing time. However, the capability...
of different metals to absorb carbon atoms depends on their carbon solubility potential. The capacity of a metal to absorb carbon atoms when in contact with a carbon source is given by Malshe et al. [41]:

\[ C(y) = C_1 \left( \text{erfc} \left( \frac{y}{2\sqrt{Dt}} \right) \right) \]  

where \( C(y) \) is the carbon concentration at \( y \) distance from the interface, \( C_1 \) is the interface carbon concentration, \( \text{erfc} \) is the error function, \( D \) is the diffusion coefficient, and \( t \) is time.

2.2.3. Graphitization of lattice carbon atoms. Carbon lattice structures can be classified as graphite, amorphous carbon, diamond, and fullerene [2]. The variation in the lattice structure results in disparate physical and chemical properties. For instance, graphite has the weakest structure and lowest hardness because of the weak van der Waals forces between the stacked layers of carbon. That is the reason why it can be easily removed when compared with any other carbon phase. On the other hand, the graphite is much more stable than any other coetaneous structure under atmospheric conditions. Thus, other carbon structures tend to transform into graphite under appropriate conditions. The key requirement for this phase transformation is to obtain sufficient activation energy to break the energy barrier between the two lattices. This activation energy can be obtained from a mechanical, chemical, or thermal energy source. A catalytic metal can significantly decrease the activation energy required to transform diamond into graphite. However, carrying unpaired \( d \) electrons is one of the prerequisites for these catalytic metals (e.g. Fe, Ni, Co, Mn, and Cr) to chemically bond with carbon instead of forming carbides [56–58]. Therefore, a diamond that comes in contact with these catalytic metals at elevated temperature loses its lattice structure and transforms into graphite or amorphous carbon. In principle, the protruding crystals on the diamond surface initially come in contact with a catalytic metal and readily converted into graphite or other non-diamond carbon. Subsequently, the transformed graphite is easily removed due to the weak binding force between layers.

2.2.4. Evaporation. If a sufficient amount of heat is applied to a material, the surface will melt or evaporate. The rapid development of laser sources, e.g. femtosecond and picosecond laser, has made this approach a reality for diamond polishing. When a laser beam irradiates the diamond surface, the local heating produces a temperature of several thousand degrees that melts and evaporates a proportion of the diamond surface. No material can survive at this extremely high temperature, even the most rigid diamond in nature. As the laser beam incidence angle increases relative to the normal direction of substrate, the illuminated area increases, and the energy density decreases. At a certain angle of incidence, a laser beam delivers more energy to the protruding regions than the rest of the substrate. That is why the protruding areas are removed faster, and a flatter surface is obtained more quickly when the laser beam incidence in the normal direction of the substrate.

2.2.5. Sputtering. High-energy ions or atoms striking a diamond deteriorate the lattice structure. The carbon atoms detach from the surface as part of a physical process called sputtering. In this process, an ion source operated with a stable current is important to obtain high processing efficiency and a high-quality diamond surface. The MRR of sputtering can be controlled by monitoring energy and the number of the incident ion beams. The sputtering rate, \( R \) (A min\(^{-1}\)), is given by [41]:

\[ R = 62.3 \frac{JSM_a}{\rho} \]  

where \( J \) is the ion current density (mA cm\(^{-2}\)), \( S \) is the sputtering yield (atoms/ion), \( M_a \) is the atomic weight (g), and \( \rho \) is the density (g cm\(^{-3}\)). The sputtering rate depends on the sputtering yield, which, in turn, depends on the nature of the material. It should be noted that the energy of incident ions must be higher than the threshold breakdown energy of the chemical bonds in diamonds.

However, there are some cases where the sputtering process can be realized below threshold energy, called chemical sputtering. It is believed that the chemical bonds of diamonds can be weakened due to thermal activation by high energy ions. For instance, the hydrogen-induced sputtering of carbon-based materials performed at low temperature was explained by H ions injecting into C–C bonds and breaking them; this mechanism was named swift chemical sputtering [30]. Sputtering also plays an important role in RIE. For example, plasma polishing with chemically active ions and radicals has a significantly higher sputtering yield compared to pure physical sputtering.

2.2.6. Chemical reaction. Numerous polishing techniques are based on the chemical reactions between diamonds and gases or liquids. By optimizing the plasma temperature, the etching process of diamond can be realized at reduced or atmospheric conditions in the open air. Argon (Ar) gas is often used to create an inert environment, whereas the addition of reaction gases, such as \( \text{O}_2 \), \( \text{H}_2 \), \( \text{Cl}_2 \), \( \text{SF}_6 \), \( \text{CF}_4 \), or a combination of them, activates the chemical etching process [35, 37, 38, 59] that removes carbon atoms from the diamond surface. The chemical etching reaction occurs with the addition of reaction gases because when the diamond’s carbon converts into \( \text{CO}_x \), \( \text{CH}_x \), or \( \text{CCl}_x \), with \( \text{O}_2 \), \( \text{H}_2 \), or \( \text{Cl}_2 \), respectively. These chemical reactions dominate material removal both in LP and reactive plasma etching.

A diamond can also react with strong oxidants at an appropriate pressure and high temperature. Typical oxidizing reagents such as KOH, \( \text{NaNO}_3 \), and \( \text{KNO}_3 \) are solid at atmospheric conditions and do not chemically react with diamond atoms. However, increasing the polishing temperature up to the melting point of the oxidizing reagent initiates a chemical reaction between the reagent and diamond to form \( \text{CO} \) or \( \text{CO}_2 \). Oxidizing reagents with low melting points were developed over time to simplify the polishing equipment. For example, a hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) solution acts as a reagent in diamond polishing, where \( \text{OH}^- \) radicals and \( \text{H}^+ \) ions contribute
to the chemical reactions [26]. At first, the generated active radicals adhere to the polishing surface to form a hydrogen-terminated surface. The carbon atoms react with the modified surface and create new chemical bonds such as C–O–H. Due to the additional shearing force induced by the polishing plate, newly formed chemical bonds break down along the C–C bond as it has the lowest bonding energy among the three bonds. These are the chemical reactions involved in most reactive contact polishing techniques, such as CMP, UV irradiation-assisted polishing, and PAP.

3. Mechanical polishing

MP of diamond was invented in the mid 14th century. It remained a trade secret for centuries because of its jewelry specific applications [60]. After being monopolized for hundreds of years, a quantitative and systematic study of diamond grinding and polishing was first reported by Tolkowsky et al [61]. After decades of development, a mature MP technology of diamond was established. MP technologies have been widely used in the commercial jewelry industry [62].

3.1. Progress in polishing technique and equipment

Figure 2 illustrates a typical MP process and a physical map of jewelry polishing equipment [30, 41, 63]. The diamond sample grinds against a rotating iron disc, known as a ‘scaife wheel’, charged with diamond grits on the matrix. A 20 mm thick and 300 mm in diameter cast iron plate rotating at a 300 rpm speed provides a linear velocity of 50 m s$^{-1}$ at the outer radius. A normal load of 1 kg is then applied to push the diamond sample against the high-speed scaife wheel. The mechanical abrasion between the grit and diamond surface removes the protruding parts of the diamond; eventually, the rough surface is flattened and smoothed.

Since the polishing plate is important to the mechanical polishing of diamond, it has attracted increasing attention in the efforts to improve the performance of the scaife wheel. The oldest method of preparing scaife dates back hundreds of years, as described in the following [62, 64]. Firstly, alcohol or methylated spirits is used to clean the scaife. Secondly, a suspension mixed with diamond grit and light oil is rubbed on the dried scaife surface to form a thin film. At the same time, diamond grit is distributed randomly over the grooves and pores within the scaife. The third step is ‘boarting’. During this step, a considerable force is applied on the rotating wheel until the color of the scaife surface changes from matt grey to dark grey or black. This method is highly subjective and based on the manufacturer’s experience, which jeweler families had kept secret until the early 20th century. An improved cast iron scaife, charged with diamond grit, was used in the Grodzinski and Wilks experiments [65, 66]. However, wear and tear of diamond grit is very common, requiring a frequent re-charge of the abrasive powder. In order to avoid interruptions and reduce the labor required for frequent abrasive charging, a new type of polishing plate bonded with a permanent diamond grit on a cast iron matrix was developed. These diamond bonded wheels are still widely used in the MP of diamonds [30]. Recently, Kubota et al [67] proposed an improved diamond grit charging method to realize a uniform protrusion height of charged grits, contributing to a high-precision MP and finally obtaining an ultra-smooth polished diamond surface. By controlling the charging time, different protrusion heights of diamond grit can be realized. Figure 3 shows laser-microscopic images of the polishing plate after charging for 10 min (figures 3(a) and (c)) and 60 min (figures 3(b) and (d)). The colors distinguish protrusions of different heights. The 60 min charging time results in a much smaller and more uniform protrusion height than 10 min. After 60 min of charging, the diamond grits are tightly pressed into the iron substrate resulting in uniform protrusions, which is essential to obtain consistent material removal and a smooth polished surface.

Except for the typical scaife method, numerous techniques have been developed to improve the polishing rate and surface quality during the MP of diamonds. Yuan et al [68] proposed an ultrasonic vibration method for diamond polishing, which can dramatically enhance the MRR. The highest MRR was obtained at 20 kHz frequency and 5.3 $\mu$m amplitude. However, no difference was observed in the surface quality of diamond polishing with or without ultrasonic vibration. Tang et al [69] developed a new polishing method that utilized a thick diamond substrate to polish CVD diamond films. It is a very simple technique that offered an MRR greater than 10 $\mu$m h$^{-1}$, much higher than traditional MP. Ralchenko et al [70] reported fast polishing of polycrystalline CVD diamond films by ultrasonic machining in a slurry of diamond particles. This newly proposed method demonstrated efficient material removal ability, reducing the surface roughness from Ra 5 to Ra 0.5 $\mu$m within 5 min of polishing. Xu et al [9] designed
a titanium-containing corundum wheel to realize a highly efficient grinding of diamond film. The XRD and transmission electron microscope (TEM) analysis of debris confirmed that both the chemical reaction of diamond with titanium and the graphitization combined with mechanical cracking accounted for the high MRR.

3.2. Material removal anisotropy

Anisotropy is the most prominent challenge of material removal during MP of single crystal diamond (SCD), which has been observed for a long time. Tolkowsky carried out the first scientific experimental research on abrading, grinding, and polishing of diamond [2]. The results show that the material removal is strongly related to the processing wheel parameters such as speed, applied load, and polished diamond orientation. Tolkowsky proposed microcleavage as a mechanical abrasion mechanism during diamond polishing and established a model based on small identical octahedral and tetrahedral shaped blocks to explain the anisotropy of material removal. According to his findings, material removal is strongly dependent on crystal orientation and polishing direction [61]. Wilks et al and other researchers confirmed and expanded on Tolkowsky’s experimental results [8]. According to the results, it is the revolution of the polishing scaife that is important for MRR, not the rotation speed, so it was not considered by Tolkowsky et al [65, 66]. A rapid increase in temperature combined with the rubbing speed during MP of diamonds is responsible for the thermal activation and mechanical chipping of the material, which is of little significance in material removal [71].

The difference in MRRs based on crystal orientation (e.g. cube, dodecahedron, and octahedron) was systematically investigated by Tolkowsky et al [30], as shown in figure 4. The maximum removal rates of the (110), (100), and (111) planes have an approximate ratio of 1:0.5:0.1, which indicates that the (110) plane is the most easily removed crystal orientation. Moreover, the MRR also varied on each plane when grinding or polishing was conducted in different directions. The peak MRR was obtained when grinding in <100> direction on (100) and (110) planes, whereas a negligible amount of material was removed when grinding in <110> direction. The MRR of the (111) plane was always shallow regardless of the grinding direction, as seen from figure 4(c). Similar experimental results were also reported by other researchers, e.g. Hitchiner et al [72], Zheng et al [73], Grillo et al [74], and so on. Therefore, to provide scientific guidance to the industry, the terms ‘soft direction’ and ‘hard direction’ were developed to describe the level of difficulty of material removal during the polishing process [30, 62]. Each crystal plane has its own

Figure 3. Microscopic images of polishing plates with different charging times: (a) 10 min, (b) 60 min, (c) section profile of A-A line, and (d) section profile of B-B line [67].
‘soft’ and ‘hard’ polishing directions. For example, the <100> direction on (100) and (110) planes is considered a soft direction, while the <110> direction on (100) and (110) planes and all the directions on the (111) plane are hard directions. Thus, diamond polishers always conduct the polishing process in soft directions, which removes a large amount of material with minimal damage to the scaife.

A brittle-ductile transition removal mechanism was introduced by Zong et al [75–77] to explain the anisotropy of the MRR by the mechanical lapping of a single crystal. It is well known that plastic grooves and scratches easily form after MP [78, 79], which indicates plastic deformation of the diamond surface under the combined effect of shear and hydrostatic compressive stresses. The schematic illustration of diamond grits being used on a diamond workpiece is shown in figure 5(a). $P_r$ is the dynamic pressure applied on diamond grit, $V_r$ is the sliding velocity between the lapped surface and grit, $2a$ is the characteristic indentation size, $\alpha_0$ is the corner angle of the grit, $a_c$ is the depth of the cut, and $a_{cp}$ is the critical cut depth in lapping. Considering the geometrical relationship of the above parameters and the fracture toughness properties, the critical cut depth for a brittle-ductile transition in MP of diamond can be expressed as follows:

$$a_{cp} = m_{ca}a_{ca}\cot\left(\frac{\alpha_0}{2}\right) \sqrt{\frac{2\lambda_0}{\alpha_0} \frac{9\psi E\gamma}{50H^2}}$$

(3)

where the comprehensive coefficient $\lambda_0 = (1–1.6) \times 10^5$, the geometrical factor of the indenter $\alpha_0 = 1.8544$, $\psi$ is the coefficient dependent on surface roughness, $E$ is Young’s modulus in Mpa, $\gamma$ is the surface energy in J m$^{-2}$ required for fracture initiation, $H$ is Knoop hardness in Mpa, $m_{ca}$ is the coefficient related to cleavage angle, and $m_{ca}$ is the coefficient dependent on orientation angle.

According to the tensile strength of diamond crystal [80], the $m_{ca}$ is given as follows:

$$m_{ca} = \sin^2(\theta - 90^\circ).$$

(4)

Expressing $m_{ca}$ is more complicated due to the symmetry properties of diamond lattices. The dodecahedral plane (110) has a twofold symmetry, so the $m_{ca}^{110}$ is given as follows:

$$m_{ca}^{110} = \frac{9}{35} + \frac{5}{35}\cos2\omega.$$  

(5)

The cubic plane (100) has a fourfold symmetry, so the $m_{ca}^{100}$ is given as follows:

$$m_{ca}^{100} = \frac{7}{18} + \frac{3}{18}\cos4\omega.$$  

(6)

The octahedral plane (111) has a threefold symmetry, so the $m_{ca}^{111}$ is given as follows:

$$m_{ca}^{111} = \frac{5}{4} + \frac{3}{4}\cos3\omega.$$  

(7)

Therefore, the absolute critical cut depths on different crystallographic planes and different orientations of the same plane can be calculated by combining the above equations. It is assumed that the diamond grit size is 0.5 µm with a constant corner angle of 90°. Young’s modulus is 1165 Gpa for (110), 1050 Gpa for (100), and 1207 Gpa for the (111) planes [81].
Fracture surface energy \( g \) is 5.3 J m\(^{-2}\), while Knoop hardness changes from 57 to 104 GPa. The cleavage angle is 144.73° for the (110), 125.27° for the (100), and 109.58° for the (111) planes \[68\].

In order to verify the established theoretical model, diamond polishing experiments were conducted. According to the experimental conditions, diamond grit size was 0.5 \( \mu \)m, and scaife rotated at 2800 rpm giving a relative velocity of 32 m s\(^{-1}\). The externally applied load on the independent diamond grit was ignored in these experiments. The theoretical and experimental results of maximal groove depths left on the rake face after lapping in different orientation angles are shown in figures 5(b) and (c). The experimental data fit well with the theoretical ones, proving the integrity of the proposed material removal mechanism. The obtained symmetry properties of the plotted curves further illustrate strong anisotropy in the maximal groove depth in different directions. Because of the agile removal of diamond material along the soft direction, the single-cut of diamond grit is larger and generates a deeper groove. These findings provide strong evidence of the anisotropy regarding material removal of diamonds during polishing.

### 3.3. Polished surface quality

Surface quality is crucial in diamond manufacturing because current industries require high-quality surfaces with minimum roughness and surface/sub-surface damage. Due to the material removal anisotropy in the MP of diamond, the polished surface quality varies significantly along different crystallographic orientations and sliding directions. It is well established that a high MRR can be obtained when polishing along the soft direction. Acquiring a similar material removal along the hard direction is challenging. However, the response of the surface quality seems to contradict the material removal. Tolkowsky's model was considered a dominant theory until high-resolution microscopes revealed a detailed micro-morphology of polished diamond surfaces. The anisotropy of diamond polishing revealed by microscopic images dates back to the 1950s \[62\]. A clear difference in diamond polishing along soft and hard directions can be seen in figure 6. The surface polished along the soft direction is much smoother than the hard direction, which contains many cracks.

Figure 7 shows the atomic force microscope (AFM) images of the polished diamond surface along soft and hard directions \[75\]. Many nanoscale grooves can be detected in the soft and hard directions of (100) and (110) planes. The surface roughness of the (110) plane in the <100> direction is about 4.5 nm, which was reduced to 2.9 nm after polishing in the <110> direction. Similar results were obtained after polishing the (100) plane, where the surface roughnesses were reduced to Ra 3.5 nm in the <100> direction and 1.6 nm in the <110> direction. Moreover, the depths of the diamond grit induced grooves along the <100> direction (figures 7(a) and (c)) are more extensive than those of the <110> direction (figures 7(b) and (d)). Corresponding surface roughnesses show that the surface quality in the hard direction is superior to the soft direction. Therefore, it can be inferred that the more material is removed in soft directions due to the higher polishing rate, which results in a rough surface finish.

The polished surface quality is affected by both the crystallographic orientation and the sliding direction. For example,
Figure 6. Microscopic images of polished diamond surface: (a) (100) plane, and (b) (110) plane [4].

Figure 7. AFM images of (110) and (100) planes polished along soft and hard directions [75].

Figure 8 shows the surface quality of a diamond substrate after polishing in different sliding directions (e.g. $0^\circ$, $30^\circ$, $60^\circ$, $85^\circ$), under a normal load 15 N, and velocity of 8 m s$^{-1}$ [82]. Numerous microscale grooves were formed on the diamond surface when lapped with an azimuthal angle from $0^\circ$ to $85^\circ$. Interestingly, a finely polished surface was obtained despite significantly deviating from the soft direction (i.e. the <100> direction for the (110) plane). Besides, a roughly polished surface with a fracture was obtained when polishing along the hard direction (i.e. the <110> direction for the (110) plane). The corresponding 3D-AFM images provided additional information about the micro-morphology of the polished surface. The surface morphologies for $0^\circ$, $30^\circ$, and $60^\circ$ azimuthal angles mainly consisted of grooves, whereas surface fractures formed when the azimuthal angle was $85^\circ$. Therefore, the azimuthal angle between the polishing direction and the <100> direction should be less than $85^\circ$ to avoid fractures. Doronin et al. [11], also reported that a surface with atomic-scale roughness could be realized by MP in the <110> direction if the polishing direction does not exceed $20^\circ$. These findings also share similarities with previous experimental results.

Recently, Kubota et al. [67] proposed a high precision MP with an iron plate charged with micron-sized diamond abrasive...
grits. The charged diamond grits with uniform protrusion height demonstrated high-quality polishing. To investigate the influence of grit protrusion height on polishing performance, two types of polishing plates were prepared by adjusting the grit charging time. Type-A was charged for 10 min and type-B for 60 min, confirming that type-B was more uniform than type-A. Polishing was performed for 60 min with an applied normal load of 9.8 N, while the both the iron plate and diamond sample rotated at a speed of 200 r min$^{-1}$. The scanning white-light interferometer (SWLI) and AFM images, shown in figure 9, were compared to differentiate the performance of the two polishing plates. As expected, the type-B plate achieved better surface quality with a surface roughness of 1.66 nm over an $80 \times 60 \mu m^2$ area (figure 9(b)) and $Ra$ 0.29 nm over a $1 \times 1 \mu m^2$ area (figure 9(d)). The uniform height of the abrasive grit protrusions induced uniform cut depths under the same normal load, eventually producing a smoother polished surface. A uniform protrusion height of diamond grit dramatically enhanced the individual participation of the abrasive grits in material removal. Simultaneously, the normal load applied on each grit and the depth of the grooves decreased, which resulted in a smooth surface polishing and low surface roughness by the type-B plate.

3.4. Material removal mechanisms

For a better scientific understanding of material removal anisotropy during MP of SCD, numerous theoretical analyses and simulation methods were reported [12, 83–86]; among them, total-energy pseudopotential calculation and MD simulation are the most famous. Jarvis et al [12] used total-energy pseudopotential calculations to explain the polishing anisotropy based on the atomistic mechanism. Simulations were performed on a single nanoscale asperity constructed on a (110) surface, which was deformed by a rigid tip. After a detailed simulation analysis, nano-groove mechanisms were proposed based on boundary conditions and chemical environments. Figure 10 shows the carbon skeleton schematic presentation of the suggested nanogroove mechanism. When the rigid tip slides along the hard directions (figure 10(a)), the forces acting during nanogrooves formation are higher than those arising duringasperity removal, offering greater resistance to the rigid tip and nonlocal deformation. In contrast, the forces that occur during nanogroove deformation in the soft direction result in local and repeatable deformation (figure 10(b)). As discussed, these are the atomic mechanistic differences occurring during nanogroove formation that are responsible for the observed anisotropy of SCD polishing.
Figure 9. SWLI and AFM images of diamond sample surface polished by different polishing plates: (a) and (c) type-A; (b) and (d) type-B [67].

Figure 10. Carbon skeleton schematic representation of suggested nano-grooving mechanism [12].

MD simulation has been applied to study diamond friction and wear mechanisms since the early 1990s. Harrison et al [83] established a simulation based on two atomically flat diamond surfaces and found that frictional anisotropy occurs at the atomic-scale. Perry et al [86] examined the nature of friction by small third-body molecules sliding over the (111) surface of a diamond, which identified that the orientation of nonspherical molecules and surface alignments would lead to high friction during the sliding process. Gao et al [85] combined AFM results and MD simulations to study friction properties as a function of load, crystal orientation, and the sliding direction of diamond. Despite the comprehensive MD simulation studies on the friction and wear characteristics of diamond, the connection between simulated and experimental atomic wear mechanisms during diamond polishing are not fully understood. In this regard, Pastewka et al [84, 87] employed MD simulations to establish an adequate investigation of anisotropic mechanical amorphization during the planarization process of diamond. Besides, the microscopic mechanism underlying the diamond polishing was experimentally investigation by applying a velocity of 30 m s\(^{-1}\) and a normal load of 10 GPa on two unsaturated diamond surfaces [62]. The produced amorphous interface layer increased steadily during sliding in the <100> direction of the (110) plane. To correlate the simulation and experimental wear process, a diamond grit with sharp edges was used to slide over amorphous carbon (figure 11). The results indicate that a part of the amorphous carbon containing sp\(^2\) and sp will be scraped off, which agrees with the experiments [88]. After a detailed analysis based on the uphill process illustrating the microscopic origin of anisotropy during the wear process, the soft and hard directions of the (110) and (111) planes are marked. Pastewka’s model and simulation revealed an in-depth understanding of the atomic mechanism of anisotropy of diamond wear during polishing.
Figure 11. MD simulation of diamond polishing: (a) change of amorphous layer with sliding time, (b) micro removal of amorphous carbon by sharp edges of diamond grit, and (c) soft and hard directions of the (111) and (110) planes [87].

Zong et al [13] performed MD simulations coupled with nano-indentation and nano-scratching to get insights into the underlying mechanisms of diamond polishing. As shown in figure 12(a), the simulation set up consisted of diamond grit and a flat diamond substrate in which a vertical force pressed the tip of the grit into the diamond substrate. The horizontally applied force moved the grit with a constant velocity of 200 m s\(^{-1}\) along the <100> direction. The simulation results revealed that the amorphization—the transformation of perfect cubic diamond lattice to amorphous carbon atoms containing sp, sp\(^2\), and sp\(^3\)—was inevitable during MP. It should be noted that the proportion of sp\(^3\) converting to sp\(^2\) increases dramatically with the polishing time (figure 12(b)), which is believed to be the dominant mechanism of material removal anisotropy during the MP of diamond. As addressed by Pastewka et al [84], the atomic material removal can be realized when the perfect diamond lattice transforms to amorphous carbon atoms. As a result, more amorphous atoms increase the MRR. Although the predicted thickness of the (100) planes in soft (4.4 nm) and hard (3.4 nm) directions is very close (figure 12(c)), an insignificant difference between the thicknesses of amorphous layers suggests that Pastewka’s model cannot explain atomistic origins of material removal anisotropy. Zong et al proposed utilizing a proportion of sp\(^3\) to form sp\(^2\) to explain the atomistic mechanism of material removal anisotropy, which aids in understanding the diamond polishing process.

The previous discussion shows that the amorphization of the diamond lattice plays a significant role in the diamond wear process. The difference in the amorphization rate is the key to removal rate anisotropy [13, 84]. Therefore, a better understanding of diamond amorphization may help researchers comprehensively study material removal mechanisms during diamond polishing. Fairchild et al [89] found that diamond lattices are likely to collapse and form an amorphous phase when the strain in diamond reaches the critical value of 16% with a corresponding density of 2.95 ± 0.10 g cm\(^{-3}\). By relating density and strain in diamonds, the amorphization of diamonds has been verified by experiments and MD simulations. At first, the high-resolution TEM (HR-TEM) images were used to precisely distinguish the diamond lattice and amorphous region within 3 nm. Afterwards, electron energy loss spectroscopy (EELS) was used to probe the specific atomic density of diamond.

Figure 13(a) shows a prominent amorphous layer (dark region) in ion-implanted diamonds, as indicated by two bright bands with widths of 0.9 µm and 1.1 µm. The corresponding density calculated with the help of EELS decreases dramatically in the amorphous zone, as shown in figure 13(b). The perfect diamond lattice region possesses a stable density of 3.52 g cm\(^{-3}\), while the density of the amorphous region ranges from 2.1 to 2.9 g cm\(^{-3}\). The diamond amorphization mechanism is explained using MD simulations of two different approaches: vacancy calculation realized by increasing the sp\(^3\) carbon atoms, and diamond lattice stretching realized by uniaxially stretching all the carbon–carbon bonds. Thus, the density ranging from 2.0 to 3.4 g cm\(^{-3}\) of diamond was created for these models. The height of the 3rd peak in radial distribution function (RDF) is a direct indicator of the crystallinity. Figure 13(c) shows the results of two approaches, where increasing RDFs with density indicates crystal growth in both cases. Finally, the MD simulations performed with conditions close to the experimental set-up is shown in figures 13(d) and (e). Initially, a diamond supercell was created in the central region with a density gradient. The RDFs were calculated according to the final structure, which fit well with the experimental observations of the intermediate interface between diamond and amorphous carbon (figure 13(b)). In conclusion, the combination of experiments and simulations provided a complementary view of the diamond amorphization mechanism, strongly related to the density. Moreover, amorphization does not occur if diamond density exceeds a critical value, even the lattice structure is highly compromised. Surprisingly, the diamond lattice shows excellent resistance to amorphization and maintains good crystallinity even after losing 16% of its atoms.

In summary, MP has played a significant role in diamond polishing for centuries. Nowadays, MP has become the most widely applied technology in diamond-related industries because of its low cost, simple equipment, and stable MRR. However, material removal anisotropy of diamond polishing remains a significant challenge. Substantial efforts were made to explain the material removal anisotropy of diamond polishing. For example, the discovery of ‘soft’ and ‘hard’ crystallographic orientation offering the highest removal rate in a specific sliding direction was one of predecessors’ key achievements. However, the prevailing mechanisms and theories were insufficient to comprehensively understand the dilemma of material removal anisotropy. The efficiency of MP is in the order of tens of nanometers per hour, which cannot satisfy the increasing demand of the industry. In addition, due to the mechanical abrasion material removal mechanism, the polished surface contains scratches, cracks, residual stress, and damages that hinder its application in areas that require high surface quality. After all, rapidly developing CVD technology to address diamond film shattering during polishing also demands modern polishing techniques with better MRR and surface quality.
4. Chemical-mechanical polishing

Since the MP of diamonds is surrounded by multiple challenges to improving material removal efficiency and surface quality, it is necessary to develop other polishing techniques for effective and high-quality diamond polishing. Highly rough surfaces and low structural strength are key challenges that limit the broad applications of CVD diamond films. CMP, also known as thermal oxidation polishing, utilizes MP in conjunction with chemicals to enhance the MRR and improve surface quality. Thornton and Wilks [30, 90] were the first to apply CMP for diamond polishing. Later, Malshe et al [41] and Kuhnle and Weis [43] further improved this technique to obtain an ultra-smooth diamond surface. This method utilizes oxidation of diamonds since the atomic oxygen can react with diamond to form CO or CO$_2$ at high-temperature, transforming diamonds into black carbon or graphite [91]. Therefore, oxidizing agents in the molten state are considered more effective for polishing CVD diamond films.

4.1. Progress in polishing technique

Figure 14 illustrates the schematic of a typical CMP process [90]. Diamond films are fixed by a holder, moving reciprocally against the rotating polishing disc. Numerous concentric grooves present on the polishing disc contain the molten oxidizing agents. The heating system maintains the temperature slightly above the melting point of the oxidizing agents. A flattened diamond surface can be obtained due to the initial mechanical cracking and subsequent chemical reaction.

The oxidizing effect plays a vital role in the CMP of diamonds, so investigating oxidizing agents has been a hot topic in CMP research. After decades of research, the family of typically used oxidizing agents expanded to include dozens of members (e.g. NaNO$_3$, KNO$_3$, KOH, KClO$_3$, K$_2$Cr$_2$O$_7$, H$_2$O$_2$, HClO, HNO$_3$, H$_2$SO$_4$, AgO, Cr$_2$O$_3$, MnO$_2$, BaO$_2$, PdO$_2$, K$_2$FeO$_4$, KmnO$_4$, Na$_2$MoO$_4$, KIO$_4$, (NH$_4$)$_2$S$_2$O$_8$, etc) [90, 92]. The typically used oxidizing agents have very high melting points. The melting points of NaNO$_3$, KNO$_3$, and KOH which are 308 °C, 324 °C, and 360 °C, respectively. Oxidizing agents with low melting points are preferred when polishing at relatively low temperatures. For example, a melting point of 130 °C can be achieved by mixing LiNO$_3$ with KNO$_3$ [90]. Likewise, an oxidation enhanced MP was conducted at 70 °C using KMnO$_4$ as an oxidant [93]. Similarly, the CMP of diamond was also performed at room temperature using an H$_2$O$_2$ solution [27]. Under the given circumstances, the evolution of polishing plates provides another insight to
improve the diamond polishing performance of the CMP process. Similar to traditional MP, the cast iron plates were initially employed for polishing purposes. Later on, other metals such as stainless steel, nickel, titanium [94], and titanium alloy [95] were also reported as plate materials in the CMP. Xu et al [96, 97] introduced an efficient diamond polishing method that utilized a corundum grinding wheel containing Fe–Ce. In recent years, ceramic disks with concentric grooves have also been used to enhance the mechanical cracking effect during polishing [16, 91, 98, 99]. Ceramics are harder and less prone to deformation than metals. As a result, ceramic plates are considered better candidates for inducing micro-cracks and corrosion when polishing in oxidizing environments.

In practice, the oxidation regent and polishing powder are usually mixed to obtain a high removal rate. Cheng et al used a slurry containing 0.4 M KMnO₄ and diamond abrasives to polish CVD diamond films. They achieved an average surface roughness of 20 nm after 4 h of polishing [93]. Yuan et al [92] investigated the polishing performance of ten different CMP slurries. They found that the slurry with potassium ferrate (K₂FeO₄) provided the highest MRR 0.055 mg h⁻¹ and the best surface roughness of 0.187 nm. Thomas et al
Mechanical polishing
CMP
Surface roughness (nm)
Polishing time (h)
2 μm
(a) (b)

Figure 15. (a) Effect of polishing time on surface roughness of CVD films when using mechanical and chemical-mechanical polishing, and (b) SEM image of the diamond surface after CMP [30, 99].

[100] used CMP with a polyurethane/polyester polishing cloth and an alkaline colloidal silica slurry to polish nanocrystalline diamond (NCD) films and achieved a polished surface with a surface roughness of 1.7 nm after 4 h of polishing. Thomas et al [101] also utilized the silica slurry to polish the (100) and (111) planes of a SCDs and obtained ultra-smooth finishes. Werrell et al [102] employed a polyester/polyurethane polishing cloth in conjunction with six different slurries to investigate the effect of slurry composition and pH value on polishing performance. They found that the properties of the slurries, including pH, composition, and particle size were the determining factors of the polishing rate. Mandal et al [103] proposed the addition of redox agents such as H2O2, KMnO4, FeONO 2, H2C2O4, and (NH4)2S2O8 to enhance the CMP of thin diamond films. The results showed that H2C2O4 had the fastest polishing rate, while H2O2 had a minimal effect on polishing. Cui et al [104] reported an improvement in the diamond polishing process using a polishing pad covered with nano-silica and nickel powder. They achieved an ultra-smooth surface with a roughness of 0.25 nm after 140 min of polishing.

Control of polishing temperature is very important since the molten oxidants are responsible for the chemical reactions occurring during the CMP of diamond. Most conventional oxidants possessing high melting points (>300 °C) require external heating during the traditional CMP process. The additional heater not only makes the equipment complex but also generates safety issues and environmental pollution. Therefore, researchers are focusing on developing oxidants with low melting points and CMP processes that stimulate the chemical reaction of diamond at room temperature, as reflected by the above literature.

4.2. Material removal rate and surface quality

Material removal efficiency and surface quality being the generic parameters to evaluate polishing performance have been reported in many studies. Since material removal is a combined effect of mechanical and chemical aspects in CMP, the MRR and surface quality are highly dependent on pressure, sliding speed, oxidizing reagent, and the corresponding temperature.

The material removal efficiency and surface quality in the CMP process are higher than in MP [91, 98, 99]. As shown in figure 15, surface roughness decreased faster in CMP compared to MP. Using the KOH and KNO3 as oxidants, the surface roughness of CVD film was reduced from 1248 nm to 95 nm after 5 h of polishing. The corresponding SEM image of the diamond surface, shown in figure 15(b), indicates no scratching or mechanical lapping related defects after CMP. The results show that the CMP possesses the potential to produce excellent finnishings of CVD surfaces more efficiently than MP. However, using oxidants with low melting points would help simplify the polishing equipment and reduce operating costs. As discussed, 0.6:1 ratio of LiNO3 and KNO3 reduced the melting point to 130 °C. The original surface roughness of diamond varying from 8 to 17 μm was reduced to 0.4 μm after 3 h of polishing with MRR ranging between 1.7 and 2.3 mg (cm² h)−1 [90].

Yuan et al [92, 105] further investigated the polishing performance of eight different oxidants (K2FeO4, KMnO4, Na2MoO4, K2Cr2O7, Cr2O3, KIO4, H2O2, and (NH4)2S2O8). The experimental results show that K2FeO4 and KMnO4 are the best oxidants in the CMP of diamond. In the case of K2FeO4 oxidant, the effect of diamond abrasive size on MRR was experimentally investigated. As shown in figure 16(a), the MRR increased with increasing abrasive size. Obviously, the MRR is higher with the oxidant than without. The presence of oxidants accelerates the chemical reaction between the diamond substrate and chemical slurry. The effects of polishing pressure on MRR and surface roughness were systemically investigated, as shown in figure 16(b). The MRR initially increased and then decreased slightly. The external pressure significantly enhanced the mechanical action without affecting the chemical reactions during CMP. The external pressure increased the number of effective abrasives at the interface of the diamond surface and polishing pad. However, after a certain critical polishing pressure, the number of effective abrasive decreased and so did the MRR. The micro topographies of the surfaces polished by MP and CMP with a K2FeO4 slurry
Figure 16. Effect of (a) diamond abrasive size and (b) polishing pressure on polishing performance of CVD films; surface topography and surface roughness after (c) mechanical polishing and (d) CMP [105].

Figure 17. (a) Effect of polishing time on surface roughness of CVD films when using different chemical slurries and (b) SEM images after CMP with KMnO$_4$ and H$_2$SO$_4$ [93].

are shown in figures 16(c) and (d), respectively. The mechanically polished surface has visible scratches induced by abrasive particles, while abrasive related scratches were not observed on the CMP surface. An ultra-smooth diamond surface with a surface roughness of 0.48 nm was obtained by the CMP process, which dramatically improved diamond performance.

The polishing performance of different chemical slurries containing 0.4 M KMnO$_4$ and abrasives were systematically investigated by Cheng et al [93]. Diluted sulfuric acid (H$_2$SO$_4$) was used to create the acidic environment to activate the oxidation of KMnO$_4$. As shown in figure 17(a), the final surface roughness of the CVD film polished without oxidants is higher than the film polished with oxidants. The combination of chemical reagents and high pressure resulted in high-quality surface polishing. For example, after polishing with KMnO$_4$ in a H$_2$SO$_4$ environment with an applied pressure of 4 kg cm$^{-2}$ (sample C), the average surface roughness was below 20 nm after 3 h of polishing. The corresponding SEM image of sample C indicates that the rough structures formed during the CVD stage were entirely removed, as shown
in figure 17(b). The results proved that KMnO₄ improved the CMP performance of diamond.

Hocheng et al. [30, 106] conducted a series of experiments on CVD diamond polishing using different chemical slurries. In order to ease the reduction reaction during diamond polishing, a suitable amount of H₂SO₄ was added to all of the slurries. The standard reduction potentials and melting points of selective chemicals are summarized in table 1. The polishing experiments were conducted at 70 °C with an applied pressure of 4 kg and a rotational speed of 200 rpm. Better surface quality was acquired using the chemical slurry containing KClO₃, K₂S₂O₈, or H₂O₂ regents, which suggests that slurries with higher reduction potentials result in lower surface roughness. The MRR also showed similar behavior, as shown in figure 18. The highest MRR (1.39 μm h⁻¹) was obtained with the K₂S₂O₈ oxidant, which possesses a high reduction potential of 1.776 V⁰⁻¹. In general, an oxidant with high reduction potential improves the surface quality and material removal efficiency in CMP of diamond films.

Thomas et al. [100, 102, 103] employed CMP to smooth NCD films. The experiments were performed at room temperature with an applied pressure of 27.58 KPa, and a rotation speed of 60 rpm. An SF1 alkaline colloidal silica containing 15%–50% SiO₂ and 4%–5% ethylene glycol was chosen as the polishing slurry. The AFM images of the NCD film surfaces at different polishing times are shown in figure 19. A very rough surface with nanocrystalline grains interlaced together to form different grain boundaries represents the initial unprocessed surface, as shown in figure 19(a). The initial surface roughness of 18.3 nm was reduced to 11 nm and then 4.5 nm after processing for 1 and 2 h, respectively. After polishing for 4 h, the NCD film surface was smoothed to a surface roughness of 1.7 nm. The polishing began with the NCD film surface peaks in contact with the polishing pad and finished when the grain boundaries were removed. The reported MRR was about 16 nm h⁻¹, which was slightly higher than traditional MP under similar conditions.

### 4.3. Material removal mechanisms

The combined action of mechanical abrading and chemical etching is responsible for material removal during the CMP of diamond. In general, the mechanical scratches and cracks are formed when the abrasives moves against the diamond surface under high pressure. The molten oxidants react with the diamond surface to form CO or CO₂ under high pressure and temperatures. The mechanical shear and chemical etching materialize throughout the diamond polishing process. Thus, the protrusions present on the diamond surface are removed, and the surface becomes smooth. Due to the chemical etching by oxidants, better material removal efficiency and surface polishing quality of diamond can be achieved by CMP compared with the MP. Most importantly, CMP eliminated the material removal anisotropy of diamond polishing because the reported chemical etching reactions of oxidants have no preference for crystalline orientation. Despite the simple and general material removal mechanisms that are involved in CMP, many researchers are exploring the mechanical and chemical interactions during CMP of diamond.

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**Table 1.** Standard reduction potentials and melting points of selective chemicals [106].

| Chemicals     | Melting points (°C) | Chemical reaction                                                                 | Reduction potential (V⁰⁻¹) |
|---------------|--------------------|-----------------------------------------------------------------------------------|---------------------------|
| KNO₃          | 334                | NO₃⁻ + 4H⁺ + 3e⁻ → NO + 2H₂O                                                     | 0.957                     |
| NaNO₃         | 308                | NO₃⁻ + 4H⁺ + 3e⁻ → NO + 2H₂O                                                     | 0.957                     |
| KMnO₄         | 240                | MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O                                                   | 1.214                     |
| KClO₃         | 356–368            | ClO₃⁻ + 3H⁺ + 2e⁻ → HClO₂ + H₂O                                                   | 1.36                      |
| K₂Cr₂O₇       | 398                | Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2 Cr³⁺ + 7H₂O                                             | 1.507                     |
| K₂S₂O₅        | 100                | S₂O₅²⁻ + 2H⁺ + 2e⁻ → 2HSO₄                                                       | 1.776                     |
| H₂O₂          | −11 (90%), −39 (70%)| H₂O₂ + 2H⁺ + 2e⁻ → 2H₂O                                                          | 2.123                     |

**Figure 18.** The MRR as a function of the chemical slurries [30].

**Figure 19.** The AFM images of NCD film surfaces against polishing time: (a) initial surface, (b) 1 h, (c) 2 h, and (d) 4 h [100].
Diamond is the hardest and most chemically inert material and is difficult to oxidize in the atmosphere at room temperature. In contrast, carbon atoms can react with oxygen to form CO or CO₂ in an oxygen-rich environment at elevated temperatures. Yuan et al. [92] proposed a material removal mechanism based on changes in Gibbs free energy, which indicates that the oxidants can reduce the energy barrier required for diamonds to change into CO₂. The chemical reaction dominating the diamond conversion into CO₂ can be described as:

\[
\text{C (diamond)} + \text{O}_2 \rightarrow \text{CO}_2, \Delta G^0 = -397.259 \text{kJ mol}^{-1}.
\]  

(9)

Because of diamond’s strong covalent bonds (C–C), the activation energy required to convert diamond into CO₂ is very high. As shown in figure 20, the material removal mechanism based on mechanical and chemical effects can be divided into two classes. Firstly, hard abrasive mechanical scratching produces stress and surface damages on the diamond surface. The C–C bonds break to form a disordered layer, which is described as C* in figure 20(a). The increased surface energy and external work result in a low reaction potential barrier between the deformed diamond C* and CO₂. Secondly, the deformed diamond C* gets enough energy from the oxidant and mechanical shear to overcome the potential barrier E₂ and quickly reacts with the strong oxidants. A general oxidizing reaction can be expressed as follow:

\[
\text{C}^* + \text{M} \rightarrow \text{CO}_2 + \text{N}
\]  

(10)

where M represents the oxidant, and N is the product of the chemical reaction.

Therefore, it can be concluded that the synergistic effect of mechanical energy and an oxidant can increase the reaction rate without increasing the reaction temperature. A harder abrasive introduces more mechanical stress on the diamond film, promoting the oxidizing reaction. A stronger oxidant also accelerates diamond oxidation.

The x-ray photoelectron spectroscopy (XPS) analysis of the diamond surface polished with potassium ferrate slurry is shown in figure 21. The results show that the C 1s peak located at 285 eV is most dominant in the spectra shown in figure 21(a). The presence of carbon, oxygen, and iron at the polished diamond surface indicates that the chemical reaction occurred. To specify the chemical reaction during polishing, high-resolution spectra of carbon, oxygen, and iron were recorded to obtain the chemical bonding environment, as shown in figures 21(b) and (c). Other than the ‘C–C’ sp³ group, which represents the diamond carbon, ‘C–O’ and ‘C=O’ groups were also detected on the polished diamond surface. These results indicate that diamond oxidation is a major mechanism in the CMP process. Other studies have confirmed the same chemical reaction during diamond polishing [105, 107–109]. As discussed, the ‘C–C’ bond is very difficult to oxidize because of the strong covalent bonding that creates a very high energy barrier. Thanks to the mechanical scratching by abrasive particles that make considerable disordered carbon atoms, which oxidize and form ‘C–O’ and ‘C=O’ groups on the diamond surface. Due to the effect of
mechanical shear, the chemically modified disordered carbon atoms are easy to remove. The preceding chemical and mechanical actions repeat throughout the polishing process until a flattened diamond surface is obtained.

To better understand the CMP of diamonds, Thomas et al [100, 102, 103] explored another possible material removal mechanism that differs from the traditional cases. The diamond surface before and after polishing was analyzed by XPS, as shown in figure 22. Strong peaks of C 1s (~285.0 eV) and O 1s (~531.0 eV) were detected from both the unpolished and polished diamond surfaces (figure 22(a)). In general, the C 1s region determine changes in the surface chemistry of diamond films during the CMP process. As reported in previous studies [39, 40], the C 1s spectra can be divided into four chemical environments: diamond (C–C, 285.0 eV), hydrocarbon (C–H, 285.5 eV), ether (C–O, 286.5 eV), and carbonyl (C=O, 287.5 eV). Comparing the XPS spectra of the unpolished and polished surfaces, shown in figures 22(b) and (c), it can be seen that CMP does not significantly change the chemical termination of the CVD diamond surface. Instead, it leads to subtle changes in the concentrations of different carbon species. It should be noted that the graphite or graphite-related defects do not develop on the polished surface. Since the experiments were conducted at room temperature without diamond abrasives, the mechanical micro-chipping and conversion to graphite were not responsible for the material removal. Therefore, it was proposed that the polishing mechanism followed the chemical reaction of silicon dioxide (SiO$_2$). As shown in figure 22(d), the possible material removal mechanism can be divided into three major sections. (a) The CMP creates the oxidation environment at the polishing interface, increasing the carbonyl and hydroxy content at the diamond surface. (b) The newly formed carbonyl and hydroxy facilitate the bonding of silica particles to the diamond surface. (c) The SiO$_2$ particles, driven by the polishing pad, produce shear energy. C–C bonds are weaker (610 kJ mol$^{-1}$) than Si–O (800 kJ mol$^{-1}$) and O–C (1077 kJ mol$^{-1}$) bonds and more likely to break under the applied shear force. As a result, the carbon atoms are removed, and the diamond surface becomes smooth.

In summary, CMP combines mechanical abrasion and chemical oxidation reactions to realize reasonable material removal efficiency and ultra-fine polishing of diamond. Using an appropriate oxidant (e.g. K$_2$S$_2$O$_8$) and optimal experimental conditions, CMP can achieve an MRR up to 1.39 $\mu$m h$^{-1}$, which is much higher than MP. The reaction between the oxidant diamond produces new chemical bonds that are easily removed by soft abrasives during polishing. After the removal of these soft products, a scratch-free diamond surface is obtained. Based on the type of abrasives used in polishing, two different material removal mechanisms were explored to better understand the CMP of diamond. However, there are still some problems that should be considered before CMP is widely applied in the polishing of diamonds or its composites. For example, high temperature is required to polish diamonds, which is due to the oxidants’ high melting points (>300 °C). The need for installed heaters inevitably increase the complexity of polishing facilities, operating costs, and environmental pollutions, which directly opposes the contemporary shift toward green, low waste manufacturing practices. Although some oxidants with low melting points have been developed, these chemicals are still harmful to the environment. The H$_2$O$_2$ solutions seem to be the right choice because of their low pollution factor and the low-temperature requirement for polishing. However, a dramatic increase in material removal efficiency is a prerequisite before the widespread application of H$_2$O$_2$, which will be discussed in section 5. Besides, the material removal mechanisms have not been studied comprehensively. For example, whether it is the material removal anisotropy or the atomic removal mechanism of

Figure 22. XPS analysis of unpolished and polished diamond surface: (a) from top to bottom; initial surface polished for 1, 2, and 4 h, (b) C 1s XPS spectra before polishing, (c) after polishing for 4 h, and (d) possible material removal mechanism [100].
a polishing process, an in-depth investigation is necessary for the industry to flourish.

5. OH radicals assisted chemical polishing

5.1. Chemical polishing with H$_2$O$_2$ solution

Polishing with H$_2$O$_2$ solutions is a state-of-the-art method to produce an atomically smooth diamond surface, which has attracted increasing attention in recent years. The possibility of using OH radicals to flatten a diamond surface by oxidation was first proposed by Tokuda et al in 2009 [26]. Afterwards, Kubota et al [27, 54, 55] proposed wet polishing a single-crystal diamond surface by utilizing a rotating iron plate immersed in an H$_2$O$_2$ solution. After 10 h of polishing, the surface roughness was improved from 2.24 nm to 0.16 nm, promoting the current method for precise smoothing of single-crystal diamond substrates [27]. Kubota et al reported a more efficient two-step polishing technique for the atomic smoothing of a SCD (100) substrate [54]. According to this technique, a high-temperature iron plate rotating against the rough diamond surface can achieve high material removal. The chemical reactions between the OH radicals and the diamond substrate realize the surface finish.

The experimental setups and results are summarized in figure 23. The experimental setups for wet polishing were kept the same except for the addition of processing baths to contain the H$_2$O$_2$ solution during the second polishing step, as shown in figures 23(a) and (b). The initial surface roughnesses of 1.13 nm and 0.5 nm were measured by the SWLI and AFM, respectively, shown in figure 23(c). The two-step polishing yielded an atomically flat surface with surface roughness less than 0.1 nm, as shown in figures 23(d) and (e). The surface flattening resulted from the absence of nanoscale grooves introduced by MP with diamond abrasives. Figure 23(f) shows the MRR of both polishing steps, in which the cross-section profiles indicate the specific material removal depth of each step. According to the cross-sectional profiles, the MRRs during first- and second-step polishing were 147.5 and 2.2 nm h$^{-1}$, respectively. The material removal during the second-step polishing is extremely low, so surface quality should be as high as possible after the first step to reduce the processing time. Finally, a crystallographically well-ordered and ultrasmooth surface obtained by a two-step polishing is shown in figure 23(g). The effects of the polishing plate, rotation speed, and concentration of H$_2$O$_2$ solution on polishing performance were systematically investigated by Kubota et al [55, 110]. The experimental results show that the concentration of H$_2$O$_2$ solution is an important factor for improving surface

![Figure 23. (a) Schematic of the experimental setup (a) first-step polishing with an iron plate at atmospheric conditions, and (b) second-step polishing with iron plate immersed in H$_2$O$_2$ solution; surface roughness (c) initial surface, (d) after first-step polishing, and (e) after second-step polishing; (f) material removal during each polishing step, and (g) high-resolution TEM image of the final polished interface showing a well-disordered lattice structure of diamond [54].](image-url)
roughness and enhancing the MRR. Although H₂O₂ solution-assisted diamond surface polishing efficiency is far from satisfactory, the atomic surface roughness and damage-free surface polishing appear promising. The nature of the chemical reaction between OH radicals and the diamond substrate is not clarified by the explanations in the reports above, which requires a detailed investigation of the removal mechanism.

The material removal mechanisms involved in OH radical-assisted diamond polishing were further investigated by numerous researchers via MD simulations [111–114]. For example, Guo et al [111, 112] used ReaxFF MD simulations to explain the atomic removal mechanism during the diamond polishing process with silicon and diamond abrasives in aqueous H₂O₂/pure H₂O. The research shows that the oxidation of the diamond surface plays a dual role in removing C atoms. First, the diamond surface absorbs O, –OH, or H to form C–O, C–OH, or C–H bonds, respectively. Second, the C atoms on the oxidized diamond surface are removed under the abrasive mechanical action of the aqueous H₂O₂. The chemical reaction alone does not remove C atoms from the diamond substrate. A few C atoms in the form of CO or CO₂ are removed by the sliding diamond abrasives, while the rest are removed by mechanical friction [113]. The C–C bonds that form between the diamond substrate and abrasive or the C–O bonds between the substrate and OH radical catalyst ease the material removal during the sliding process. Shi et al [114] assumed that friction plays an essential role in diamond polishing, while aqueous H₂O₂ significantly changes the interfacial environment between the diamond substrate and abrasives by reducing the friction coefficient through surface adsorption. According to the MD simulation results, new bonds formed on the diamond surface in the presence of H₂O₂ catalyst contributes to the abrasive induced material removal. This may explain why Kubota et al obtained an extremely low MRR of 2.2 nm h⁻¹ in the presence of H₂O₂ catalyst. In the absence of abrasives, only the frictional effect between the rotating iron plate and the modified layer on the diamond substrate contributes to the material removal. Nonetheless, a slow chemical reaction between the diamond substrate and OH radicals results in a very low material removal on the diamond surface.

5.2. Chemical polishing with ultraviolet/vacuum-ultraviolet irradiation

Watanabe et al [29] proposed an UV irradiation assisted ultraprecision diamond polishing process based on the ability of UV-induced photochemical reactions to produce active species, such as OH and oxygen. In this process, material removal occurs when the top of the diamond substrate is oxidized to form CO and CO₂ at high localized temperatures. Experiments we conducted on single-crystal and polycrystalline diamonds using the apparatus shown in figures 24(a) and (d). The MRR of the (100) plane with UV irradiation was 0.5 μm h⁻¹, which was higher than the 0.3 μm h⁻¹ MRR without UV irradiation at 1.0 MPa. The material removal anisotropy during diamond polishing with UV irradiation was also verified based on the 2–3 times higher material removal in the soft direction than in the hard direction. After polishing for 2 h, the surface roughnesses of the (100) and (111) planes, measured by SWLI, were improved to 0.2 nm (figure 24(b)), and the (111) plane was improved to 0.34 nm (figure 24(c)). A 13 × 13 × 1.5 mm CVD diamond film formed on cemented carbide was used to conduct the UV light during the polishing experiments. As shown in figure 24(e), the stacked grain boundaries and rough structures formed during the CVD process were eliminated after 24 min of UV polishing. The final surface roughness measured by SWLI was improved to 0.35 nm, as shown in figure 24(f). The measured roughness of the (111) plane was improved to 0.2 nm, and the (100) plane was improved to 0.3 nm.

![Image of polishing setups and SEM images](image-url)
MRR with UV irradiation was 0.56 μm h⁻¹, which is four times higher than the MRR of 0.14 μm h⁻¹ without UV irradiation.

A few years later, Kubota et al. [115] developed an improved single-crystal diamond planarization method assisted by vacuum-ultraviolet (VUV) irradiation. Figure 25(a) shows the schematic of the VUV irradiation polishing apparatus. In contrast to the UV polishing, the VUV irradiations on the polishing plate surface removed the organic contamination and continuously developed a clean hydrophilic surface. The chemically active species formed on the polishing plate modifies its surface. Subsequently, the modified rotating plate comes in contact with the diamond surface, and a tribo-chemical reaction occurs that removes material from the diamond surface. The polishing experiments were conducted with and without VUV radiations under constant experimental conditions such as an applied load of 2 kg, polishing time of 1.5 h, and rotation speeds of the polishing plate and diamond sample at 200 and 1000 rpm, respectively. As seen from figures 25(b) and (c), a diamond surface free of nana-grooves with the surface roughness of 0.05 nm was obtained after VUV radiation assisted polishing. The surface polished without VUV shows visible grooves. The MRR was determined after polishing with and without VUV irradiation, as shown in figures 25(d) and (e). The material removal depths with and without VUV irradiation are 357.1 nm and 50 nm, where the removal rate for the case of VUV assisted polishing is seven times of the conventional polishing. It should be noted that the MRR of 238.1 nm h⁻¹ obtained by the VUV irradiation method is approximately 7–100 times higher than those combining the H₂O₂ assisted chemical reactions for polishing [54, 55].

According to Kubota et al., the interactions between the active species and diamond substrate are responsible for the high efficiency MRR in UV/VUV assisted polishing. As shown in figure 26(a), once the VUV irradiates the surface, the OH radicals adhered to the sapphire plate surface form Al–OH bonding groups and activate the surface. Once the modified plate moves against the diamond surface, the active OH radicals cover the diamond substrate. A chemical reaction occurs during the relative movement of modified surfaces, where H and OH bond together and release H₂O molecules, as shown in figure 26(b). Therefore, C–O–Al chemical bonds formed during the polishing process, as shown in figure 26(c). Due to the mechanical friction, the C–C bonds with the lowest bonding energy easily break easily, ensuring the removal of C atoms, as shown in figure 26(d). These chemical reactions...
Figure 27. Experimental setup and results of SCD (100) PAP process: (a) schematic of the PAP apparatus, (b) optical emission spectroscopy (OES) of Ar based plasma, (c) surface roughness before the PAP process, (d) and (e) surface roughness after PAP using a quartz glass polishing plate, and (f) surface roughness after PAP using a sapphire polishing plate [28].

Yamamura et al [116] proposed a PAP method to fabricate a damage-free diamond surface. The PAP is an abrasive-free diamond polishing technique that ensures high quality polished surfaces. Due to the chemically reactive nature of the plasma-induced species, the material removal efficiency is promising when PAP is applied to ultra-hard materials, such as silicon carbide, sapphire, gallium nitride, aluminum nitride, etc [117–119]. Recently, Yamamura et al [28] reported a remarkable diamond polishing process with an MRR of 2.1 µm h⁻¹ and surface roughness of 0.13 nm by employing this state-of-the-art technology. A schematic of the polishing principle of PAP is shown in figure 27(a). In PAP, the generated plasma contains OH radicals that adhere to the polishing plate and modify its surface. The optical emission spectra of Ar plasma, shown in figure 27(b), indicates the generation of OH radicals. The material removal occurs in PAP when the chemically modified plate eliminates C atoms as it comes in contact with the rotating diamond surface. After employing PAP with quartz as a polishing plate, the surface roughness of diamond with step structures was improved from 54 to 0.46 nm, as shown in figures 27(c) and (d). However, dozens of nanoscale scratches still can be observed on the polished surface, as shown in figure 27(e). Quartz glass is softer than diamond substrates and produces SiO₂ particles that act as abrasives during the polishing process and induce scratches on the surface. In order to minimize scratches, a sapphire polishing plate was used to polish the diamond surface. PAP with a sapphire polishing plate produced a scratch-free and smooth diamond surface. The surface roughness improved from 5.47 to 1.79 µm, as shown in figure 27(f). Furthermore, the Raman spectroscopy measurements shown in figures 27(g) and (h) indicate that PAP is a stress and phase transformation-free polishing technique that can realize damage-free SCD processing.

Recently, the MRR of PAP was improved to 13.3 µm h⁻¹ by adding O₂ gas to the plasma reactive gas [120]. As shown
in figure 28, the developed PAP method is applied to polish a 20 mm square large mosaic SCD substrate, the result of which indicate that PAP completely removed and planarized the CVD-grown mosaic SCD substrate. A smooth diamond surface with a width less than 0.5 μm was obtained by applying PAP to the polishing of a CVD-grown mosaic substrate. The high MRR and good polished surface quality of PAP make it a promising technique to replace traditional coarse and fine polishing.

Material removal in the PAP process was explained based on the following surface modification mechanisms: (a) oxidation or fluorination and (b) O or OH termination. The former was confirmed by the oxidation of silicon carbide (SiC) and fluorination of gallium nitride (GaN) using PAP. During PAP, the hard crystal lattice layer was converted to a soft layer, which was subsequently removed without damaging the surface. The latter was verified during the PAP of single-crystal sapphire, where the hydration or OH termination of the topmost sapphire surface is believed to be responsible for the MRR of the sapphire c-plane. Therefore, the material removal mechanism of SCD in PAP can be described as follows. Firstly, the discharge modifies the topmost surface of the sapphire plate by inducing OH termination. Secondly, the C–O–Al bond formation is accomplished at the interface of the OH terminated polishing plate and the diamond surface. When the diamond rotates relative to the polishing plate, the bonded carbon atoms are removed without causing any graphitization or amorphization.

In summary, realizing the atomic scale smoothing and damage-free finishing of diamonds by utilizing chemical reactions between active plasma species and diamond surfaces, instead of abrasives, is a key advantage of the modern finishing methods over conventional processing techniques. Low-cost and simple processing at the atmospheric conditions further contributes to the key features and viability of these methods. Meanwhile, the material removal efficiency of H₂O₂ solution or UV/VUV assisted polishing scaled from 2 to 240 nm h⁻¹ is difficult to satisfy the increasing demand for ultra-smooth diamond surfaces. Therefore, the machining efficiency of these techniques should be improved to promote their widespread applications. Although PAP looks promising with a material removal efficiency of up to 2.1 μm h⁻¹, the complex machining facilities inhibit its widespread application. Moreover, the existing MD simulations of the OH radical assisted polishing are still very weak and require further investigated to better understand the material removal mechanism during polishing.

6. Dynamic friction polishing

Temperature plays an important role in diamond polishing, especially when the conversion of diamond carbon to graphite or amorphous carbon is involved in material removal. The graphite and amorphous carbon are easier to remove than diamond carbon. Although the conversion of diamond carbon
to non-diamond carbon requires very high temperatures, it can be achieved at relatively low temperatures (<700 °C) and low atmospheric pressure with the addition of catalysts, such as metals with unpaired d electrons. The rapidly growing market demands ultra-smooth diamond surfaces, which is only possible with the development of efficient and low-cost polishing technologies. DFP was developed under this context. DFP utilizes frictional force to produce sufficient heat at the interface of the high-speed metal polishing plate rotating against the diamond workpiece under a heavy load. Appropriately high temperature promotes the conversion of diamond carbon to non-diamond carbon, which is either mechanically removed by the rotating metal plate or oxidized and evaporated in the form of CO or CO₂ gas.

6.1. Progress in polishing technique

DFP is a relatively new diamond polishing technology, which was first reported in the mid 1990s by Kiyoshi Suzuki and his colleagues [18, 121], and further improved by Chen and Zhang [17, 23, 47–53]. Figure 29 shows a rotating metal disk conducting the DFP of the diamond workpiece. A high mechanical load is applied on the rotating disk to produce a considerable amount of heat when the plate comes in contact with the diamond surface. The heat produced at the interface activates the thermo-chemical reaction of diamond that promotes the conversion of diamond carbon to non-diamond carbon. The non-diamond carbon is either mechanically removed by the rotating metal plate or evaporated in the form of CO or CO₂ gas after oxidation. This approach has the following advantages: abrasive-free, simple processing at environmental conditions, and high removal rate due to the ease of mechanically or thermo-chemically removing non-diamond carbon. Catalysts such as Fe-based metals and stainless steel (SUS 304) are used to promote convert diamond carbon to non-diamond carbon at low temperatures. In general, the catalytic plate can be made of one or a combination of following metals: Al, Cr, Mn, Fe, Co, Ni, Cu, Pt, Ti, V, Zr, Mo, Ta, and W.

Since catalytic metals can activate the chemical reaction of diamonds, significant efforts have been made to find reasonable catalytic elements. Kiyoshi et al. [46] developed a DFP process based on SUS 304 disc and investigated the material removal efficiency in different environments. The DFP experiments were conducted on a vertical machine center, where the SUS 304 disc was driven by a spindle, and the diamond was fixed on a linear motion guide. When the diamond is moved to contact the rotating disc, the normal force can be acquired by tool dynamometer. Because of the large applied pressure and fast sliding speed, a spark is produced due to the frictional heating during the DFP process. By keeping other experimental conditions such as \( V_s = 2500 \text{ m min}^{-1} \), \( P = 100 \text{ MPa} \), \( V_p = 150 \text{ mm min}^{-1} \), and \( L = 10 \text{ mm} \) constant, the polishing efficiency was systematically investigated in Ar, O₂, Air, and N₂ environments. The polishing was performed for 30 s in Ar, Air, and N₂ environments and 15 s in O₂. The material removal efficiency in the O₂ environment was the highest among the four gases. The elevated temperature in the O₂ environment is sufficient for converting diamond carbon to CO and CO₂, which quickly evaporates from the diamond surface resulting in high material removal during DFP. High material removal is also evident from the SEM images of the diamond surface taken before and after DFP polishing in the open air environment.

By pointing out the unpaired d electrons, the vertical alignment principle, high hardness, and oxidation resistance at elevated temperatures are basic requirements for a polishing plate. Yuan et al prepared an FeNiCr alloy polishing plate to improve diamond polishing performance (figure 30(a)) [122]. They prepared the FeNiCr alloy polishing plate using mechanical alloying and hot-press sintering. Figure 30(b) shows the XRD of FeNiCr, which indicates that the main component of the plate is C_{0.10}Fe_{0.73}Ni_{0.17}. However, the presence of TiC and ZrO₂ peaks in the sintered material is due to the mechanical alloying and milling processes. Because of the similarity of as-sintered FeNiCr alloy and SUS 304, except the TiC and ZrO₂ phase, the oxidation resistance is compared to the SUS 304. After oxidizing for 80 h at 1000 °C in air, the as-sintered FeNiCr alloy exhibits better anti-oxidant performance than SUS 304 (figure 30(c)). Moreover, the MRR of the FeNiCr alloy polishing plate is much higher than that of TiAl, SUS 304, and the cast-iron plate (figure 30(d)). The thermal oxidation reaction between carbon and oxygen and carbon diffusion into the metal plate is important for material removal during the DFP process. The excellent anti-oxidant property of the polishing plate also contributes towards the preceding chemical processes during DFP. The oxidation reaction between metal and oxygen reduces the number of metal atoms with unpaired d electrons, which lowers the chance of further thermal oxidation. As confirmed by anti-oxidation experiments, the as-sintered polishing plate exhibits high resistance against the oxidation process at high temperatures in the ambient atmosphere. Therefore, the MRR of the as-sintered FeNiCr alloy polishing plate is almost seven times higher than that of conventionally used materials.

According to the key importance of the metal catalyst in promoting the chemical reaction during DFP, many metal-based polishing plates were reported. Huang et al [94] developed a low-pressure DFP process based on a super-high-speed rotating titanium plate and obtained an MRR of 12 \( \mu \text{m h}^{-1} \) at 0.3 MPa pressure. The same groups also
developed a new kind of stainless steel, 0Cr18Ni9 [122], which reached an MRR of 36–51 µm h\(^{-1}\) with 100 m s\(^{-1}\) polishing speed and 0.17–0.31 MPa pressure. The XPS analysis indicates that the chemical reaction between carbon and titanium/stainless steel and carbon diffusion into the polishing plate are both responsible for high-efficiency material removal. Shi \textit{et al} [123] developed two kinds of manganese-based alloys, Mn–Cu and Mn–Ni, to achieve high quality and high-efficiency polishing of diamond. The results show that the Mn–Ni alloy offers a higher material removal efficiency of up to 1.45 µm h\(^{-1}\) than Mn–Ni alloy with 0.22 µm h\(^{-1}\) under the same experimental conditions. Xu \textit{et al} [96, 97] proposed a high-efficiency smoothing technique of CVD diamond film by adding the iron and cerium into a corundum grinding wheel. According to the results, the MRR reached 11.60–190.77 mg h\(^{-1}\) at a grinding speed of 200–500 rpm. After grinding, the TEM analysis of debris shows traces of graphite and Fe\(_2\)C, indicating the conversion of diamond into graphite and the chemical reaction between Fe and C, which contributed to high material removal. Recently, Cui \textit{et al} [104] proposed a polishing method based on nano-silica and nanonickel powder. The results show a high-quality surface that can be obtained with a surface roughness of 0.25 nm measured from a 50 × 50 µm\(^2\) area after polishing by nickel powder. Raman spectroscopy analysis shows that the nickel powder acts as a catalyst, promoting the graphite polishing process.

Zheng \textit{et al} [124] reported a high-speed three-dimensional DFP method to prepare ultra-smooth diamond. According to the Raman spectrum analysis, the subsurface damage induced by the tribology action at high sliding speed (35.8 m s\(^{-1}\) or above) is located at a greater depth and consists of two layers.

### 6.2. Material removal rate and polished surface quality

The remarkable advantages of the DFP technique are ultra-high MRR and fast reduction in the surface roughness of diamonds from several microns to a few hundred nanometers. Studying how the processing parameters affect the MRR and surface quality can give diamond polishers comprehensive guidance for selecting optimal experimental conditions. In the last two decades, numerous studies have been reported on this issue.

Chen \textit{et al} [17, 49] established the polishing map of polycrystalline diamond composites (PCDCs) by systematically investigating the effect of polishing conditions, e.g. applied pressure and sliding speed on the polishing rate. They used two different PCDCs workpieces: type 1 containing 95% diamond grains, and type 2 containing 70%–75% diamond grains. Figure 31 shows the variation in the polishing rate under different pressures and sliding speeds. The polishing rate increased with pressure and sliding speed, which are important phenomena that contribute to material removal during the
DFP process. High pressure and fast sliding speed inevitably generates heat and high temperatures at the polishing interface, which ultimately improves the conversion of diamond atoms to graphite. The polishing rate increased dramatically when applied pressure and sliding speed enhanced the effects of both mechanical and chemical mechanisms. Figure 31(b) shows the cracking that appeared on the type 2 workpiece when high polishing pressure or fast sliding speed was selected during the DFP process. The lower content of diamond (70%–75%) in type 2 PCDC reduced the strength of the workpiece, which is why it is easy to produce cracks on type 2 workpiece under high pressure or fast sliding speed.

Figure 32 shows the SEM images of two different PCDC workpieces before and after polishing. For better observation of the surface morphology, images were captured after tilting the specimen to 52° inside the SEM chamber. The surface roughness of the type 1 PCDC was reduced from 4 to 0.3 µm within 6 min of DFP processing at 5 MPa pressure and 30 m s⁻¹ sliding speed (figure 32(b)). After DFP processing, diamond grains with dimensions of several to a 100 microns were observed on the surface. In addition, wear traces appeared on the diamond surface, probably caused by the mechanical action of the polishing plate. To avoid cracking of the type 2 PCDC workpiece, a pressure of 3.1 MPa and a sliding speed of 20 m s⁻¹ were selected. After DFP processing for the same polishing time, the initial surface roughness of ∼1.7 µm was reduced similarly to the type 1 workpiece. In contrast to the type 1 PCDC workpiece, uniform diamond grains with an average size of tens of microns were observed after DFP processing, which is why low pressure and slow sliding speed are preferred in polishing. The capability of DFP to quickly produce high quality surfaces on both PCDCs is another advantage of polishing methods that utilize a high content of diamond grains. The polishing damages were further studied at the atomic scale by cross-sectional TEM analysis, shown in figure 33. The TEM sample was taken from a type 2 PCDC polished workpiece [23, 30, 53]. A 20 nm width layer attached to the diamond lattice layer could be observed in the low resolution TEM image. The EELS shown in figure 33(b) confirmed that the main phase of the
attached layer is amorphous carbon. The mechanical stress and thermal-chemical reactions may convert the diamond carbon to amorphous carbon. The HR-TEM images show that the lattice structure of the diamond is very different from the formed amorphous layer. It is easy to understand why such an amorphous carbon layer forms during the DFP process. High pressure and fast sliding speed are applied during polishing to obtain sufficient heating to activate the thermal reaction. The diamond lattice easily converts to amorphous carbon atoms under such high stress, temperature, and friction.

6.3. Material removal mechanism of DFP

The possible material removal mechanisms of DFP are summarized in figure 34. High polishing speed and pressure during the DFP process produce frictional heating and increase the temperature at the interface. When the temperature rises above 700 °C, a proportion of the lattice carbon atoms converts into graphite due to the chemical and mechanical effects occurring at the polishing interface in the presence of a metal catalyst plate. Graphite carbon is easy to remove, either mechanically or chemically. The literature discusses three types of carbon atom removal modes of DFP [47, 48]. Mechanical abrasion easily detaches the deformed and transformed carbon atoms from the diamond surface. Due to the metal plate catalyst, a part of the non-diamond carbon oxidizes and escapes as CO or CO₂ gas. Some carbon atoms diffuse into the metal disk until the carbon solution of metal is saturated.

The thermal-chemical reaction between the diamond and the metal catalyst is responsible for high-efficiency material removal during the DFP process. At atmospheric pressure, diamond is an unstable form of carbon, which can be efficiently converted to graphite at temperatures above 1700 °C [125]. However, the conversion temperature can be lowered to about 700 °C in the presence of an iron catalyst [49]. As discussed, the frictional heating produced under high pressure and fast sliding speed can raise and maintain temperatures above 1000 °C. Chen et al [50] established a mathematical model based on the Greenwood–Williamson’s statistical asperity model and Jaeger’s moving heat source analysis to predict the interface temperature during the DFP process. By calculating the number of asperities and the contact area, the temperature due to friction at the interface of diamond asperities and the metal surface can be calculated from the following relation:

$$T = \frac{13.18pi a h}{46.85K_p + 9\pi K_d \sqrt{\frac{\pi (0.87 + P_e)}}}$$

(11)

where $a$ is the average contact radius of the asperity, $h$ represents average heat flux at the real area of contact due to the frictional heating, $K_p$ is the thermal conductivity of polycrystalline diamond, $K_d$ refers to the thermal conductivity of the polishing disk, $P_e$ is the Peclet number of the polishing disk material. The effects of processing parameters (e.g. surface roughness, material properties of diamond, polishing velocity, and polishing pressure) on temperature were systematically investigated based on the established model. The results show that increasing the polishing speed is the most effective way to improve the polishing interface temperature.
In summary, the material removal efficiency of DFP is highest among the existing diamond polishing techniques. Whereas no material removal anisotropy is observed due to the chemical reaction based material removal mechanism. These advantages make DFP a suitable approach to treat rough CVD diamond films, decreasing the surface roughness from microns to tens of nanometers within a few seconds. However, a proper temperature to activate the chemical reaction between the metal plate and diamond requires a very high load and fast sliding speed. Since the metal plates are susceptible to melting at high temperatures, the polished diamond surface always contains an adhered metal layer that is very difficult to remove. This eventually leads to an unsatisfactory surface quality after DFP. While current studies focus on the processing of this technique, the explanation of the material removal mechanism is far more satisfactory. Both the mechanical and chemical aspects contribute to material removal during DFP, but the dominate mechanisms remain unclear. Furthermore, explaining the material removal mechanism at the atomic level requires a comprehensive understanding of the mechanism driving ultrafast material removal of DFP.

7. Ion beam polishing

According to the material removal mechanisms, IBP can be divided into ion beam bombardment [40, 126–128] and plasma beam etching [129–131]. Ion bombardment utilizes physical ion sputtering to remove diamond atoms. In plasma etching, the chemical effect of incident reactive ions removes atoms from the diamond surface. In most cases, material removal generally involves a combination of these two mechanisms.

7.1. Ion beam sputtering

In 1972, Spencer et al [40] reported the ability of argon-ion beams to simultaneously mill a hole in diamond and polish the inner surface. This was the first-ever experimental report on diamond polishing by IBS. Ten years later, Taniguchi et al [126] investigated the polishing performance of ion sputter-machining of a diamond surface both experimentally and theoretically. Hoffman et al [127] observed different carbon atom structures with different ion beams. With a combination of argon and oxygen ion beams, Zhao et al [128] successfully reduced the surface roughness of a diamond film from 6 μm to 217 nm. Bertrand et al [132] achieved an optically smooth diamond-coated film surface with surface roughness below 5 nm by the developed ion-assisted polishing system. Koslowski et al [132] studied the surface morphology evolution of a diamond (100) surface with low-energy (1.2–1.5 keV) Ar⁺-ion bombardment and obtained a minimum surface roughness of 4.5 nm. Ostrovskaya et al [133] found that diamond wettability can be tailored in a broad range after ion bombardment. The bond transformation from sp³ to sp² during ion polishing results in a hydrophobic surface.

Takashi et al [134] reported nano-smoothing of SCD chips by 1 keV Ar⁺ ion bombardment at different incident angles varying from 30° to 80°. The initial surface roughness of 1.2 nm was reduced to ~0.1 nm, in 60 min. As shown in figures 35(a)–(d), a smooth diamond surface was obtained when the incident ion beam was positioned at less than 30°. However, the polished surface became rough when the incident angle increased from 45° to 80°. In addition, the effect of ion dose on the processed surface roughness is shown in figures 35(e)–(h). The surface roughness of the diamond chips increased with increasing ion doses when the surface was irradiated with a 1 keV Ar⁺ ion beam incident at 60° and 80° angles. A theory based on the Bradley and Harper model and equations were developed to explain the smoothing and roughening mechanisms. Regardless of the high initial surface roughness of the diamond chips, the diamond surface roughness was reduced to 0.1 nm by choosing the proper process parameters. Ishikin et al systematically investigated the effect of accelerated gas-cluster ion bombardment on the diamond surface [135]. They achieved a smooth diamond surface using a dose of 10 keV gas-cluster ions above 10¹⁶ cm⁻² can.

In IBS, the diamond surface is irradiated by ions at a certain incidence angle, resulting in the physical removal of the diamond carbon atoms [41]. Initially, the ion beam induces localized heating at the diamond surface. Once a beam with sufficient energy impacts the diamond surface, the ions overcome the surface potential barrier, penetrate several surface layers of the solid, and neutralize after colliding with the diamond atoms. The kinetic and ionization energies of ions heat the surrounding lattice. Consequently, one or more of the host lattice atoms are sublimated [30]. Wang et al [134] demonstrated that energetic Ar⁺ ions transformed diamond phases by changing the sp² and sp³ hybridization ratio. Michael et al [136] established an atomistic/continuum multiscale model to explain the ultra-smoothing of diamond-like carbon. It is believed that ions impacting at the atomic scale induce downhill currents. These currents immediately smooth the initially rough substrates by eroding hills into neighboring hollows at the continuum scale. This newly developed theory can explain ion polishing of diamond surfaces. The characteristics of a single ion impact on ta-C films were discussed using quantum MD simulations, the results show a small crater (the right insert in figure 36(a)) that appeared in the film when it was implanted with a new atom. MD simulations were also used to calculate the specific impact induced average change in the local surface profile after consecutive impacts from 1000 atoms (figure 36(a)). The impact induced height change decreased with increasing distance from the impact point. Ion beam induced decay of a sine shaped ta-C surface is further discussed to show the evolution of surface carbon atoms. The insert in figure 36(b) shows carbon atom movement after the impact of 4000 C atoms with 100 eV kinetic energy. It should be noted that the initial sine-shaped surface became completely smooth after the impact of the ion beam.

The most appealing quality of IBS is the physical nature of material removal, which never changes the physical or chemical properties of the polished materials. Atomic processing makes IBS a suitable technique for a wide range of applications that rely on focused ion beams (FIBs), such as the ultra-precision machining of diamond films. The MRR is unsatisfactory due to the ion beam’s relatively small
Figure 35. AFM images of a polished diamond surface irradiated by 1 keV Ar\(^+\) ion beam: (a)–(d) dependence of surface roughness on different incident angles; (e)–(h) dependence of surface roughness on different ion doses [134].

Figure 36. (a) The dependence of impact-induced height variation on the distance from the impact point. The insert pictures reveal the formation of a carter after impact by a new atom (black sphere), a snapshot of the initial configuration (left), and the formation of a small crater after 1 ps (right). (b) Ion-beam-induced decay of a sine-shaped ta-C surface. The graph plots the power spectral strength of the relevant Fourier mode as a function of film thickness \(S\) for two ion energies: 30 eV (noisy red curve) and 100 eV (noisy blue curve). Snapshots of the initial system (lower left) and after the impact of 4000 C atoms with 100 keV kinetic energy (upper right) [136].

dimension. However, FIB can dramatically improve the material removal ability, which is useful for polishing and processing microstructures in diamond surfaces. In practice, applying IBS at the final processing stage can help prevent damaged or contaminated layers from forming in the polished diamond surface. However, the cost of the corresponding machining facilities is very high due to the sophisticated ion source and complex vacuum chamber.
72. Plasma beam etching

Diamond etching can be realized at reduced or atmospheric pressure in the air under appropriate temperatures. Evans et al [34] were the first to study the air constituents responsible for diamond surface etch pits. Sandhu and Chu [35] studied the RIE of diamond films using O₂ and H₂ gases. The results show that plasma produced with different reactive gases altered the type and density of the reactive species. Whereas a higher plasma etching performance was observed with O₂ than H₂ under the same experimental conditions. The diamond etching rate obtained for O₂ ions having 0.4 keV energy is about 0.3–0.4 nm min⁻¹, much higher than ion beam bombardment. Vivensang et al [36] performed RIE smoothing of a diamond surface by SF₆–O₂ plasma and reported a reduction in the surface roughness from 40 to 14 nm. Shpilman et al [37] proposed an oxidation and etching process of CVD diamond by thermal and hyperthermal atomic oxygen. As a non-contact polishing technique, Sichen et al [24] found that ion beam etching can remove subsurface damages and promote diamond surface self-healing.

Naamoun et al [38] studied the mechanism of etch-pit formation on diamond surfaces etched with H₂/O₂ plasma. Their results indicate that the misorientation angle of the diamond crystal surface strongly influences the shape of the etch pits. For the etching process conducted in the <100> direction, macro-steps were observed on the polished surface, leading to high surface roughness (figures 37(a) and (b)). In contrast, a smooth diamond surface without etching pits was obtained after etching in the <110> direction (figures 37(c) and (d)). The diamond surface can be polished to very low surface roughness (15 nm) when etching is conducted in the <110> direction on a surface with a misorientation angle less than 20°, as illustrated in figure 37(d).

According to Nobuteru et al [39], etch pits are mostly formed along the edge of the <110> direction, and the majority of them look like an inverted-pyramidal hollow with two types of shapes: point-bottom and flat-bottom. Figure 38 shows the evolution of etch pits on the etched depth. The scratches induced by MP evolved as flat-bottom etch pits and grew in diameter with increasing etched depth, as shown in figures 38(a)–(c). As the etching proceeds, the 10 μm-deep flat-bottom pits vanished, while only the point-bottom pits remained, as shown in figure 38(d). This is because the etching mechanically deformed carbon atoms is easier than etching lattice atoms. Alexandre et al [137] also obtained two similar etch pits caused by dislocation differences. The same etch-pits were also observed by Achard et al [138], where mechanical induced scratches mostly caused the flat-bottom pits. According to the experimental results, etching rates depend on crystallographic orientations.

According to Ma et al [59], electron cyclotron resonance plasma producing O₂ ions are believed to be a potential candidate for CVD diamond film polishing. The polishing results show that the diamond surface ridges were preferentially etched, reducing the surface roughness from 3.06 to 1.08 μm within 4 h (figure 39). Crawford et al studied the effect of hydrogen plasma power input on the etching performance of a (100) diamond surface roughness [139]. They achieved an ultra-smooth 3 × 3 μm² surface with a roughness of 0.2 nm using tailored Cl₂ + Ar and O₂ + Ar plasma chemistries.

The chemical reactions in reactive plasma beam etching are more effective for material removal than physical ion bombardment. Continuous ion bombardment produces sufficient
local heating to activate the chemical reactions. Then, existing reactive species, such as O, O$_2$, O$_3$, OH, and H, interact and remove carbon from the diamond surface via heterogeneous chemical reactions. Thus, the MRR of RIE is much higher than that of IBS. It is believed that the etching process started at the point of dislocation and then extended along the
dislocation line [38, 138]. The etching rate is faster along dislocations because dislocations fracture the bonds between carbon atoms, which are responsible for maintaining complete lattice structures. This may be the reason why etch-pits were always observed after RIE. Obtaining an ultra-smooth diamond surface with atomic scale surface roughness is challenging because it is impossible to obtain dislocation free diamond samples under the existing technological conditions.

Currently, RIE polished surface quality does not meet practical application requirements. However, low surface quality does not affect its outstanding material removal potential in diamond polishing. As a typical non-contact and stress-free polishing method, RIE is suitable for processing thin diamond films. However, after RIE, the residual etched pit problem should be solved before it can be widely applied for diamond polishing. The formation of etch-pits is related to dislocations. However, the formation mechanism is unclear. Nonetheless, a comprehensive understanding of etch pit formation can help remedy this discrepancy and ensure ultra-smooth diamond polishing. Simultaneously, the chemical bonding theory at the quantum level should elaborate on the atomic material removal mechanisms during RIE of diamonds.

8. Other polishing techniques

8.1. Thermochemical polishing

In the middle of the 20th century, Grodzinski et al [30] proposed a diamond polishing method assisted by a hot-metal-plate, called TCP. This method involves an iron or nickel polishing plate heated above 750 °C. It is believed that the hot metal plate melts the carbon atoms, transforming a rough diamond film surface into a smooth, glossy surface [140]. Initially, this method was used to polish the single crystalline diamond tools used in the jewelry industry. However, due to the vast development and application of CVD diamond films, TCP gained popularity outside of the jewelry industry. Yoshioka et al further improved the process [7, 32].

The typical experimental setup of TCP is shown in figure 40 [15, 141]. Polishing is performed by rotating the diamond sample against a metal plate under external pressure. The entire process is conducted in an evacuated, reductive, or inert gas environment at a high temperature (>700 °C). Compared with conventional MP, both the workpiece speed and polishing pressure are kept extremely low. After detailed research and multi-testing, Weima et al [15] concluded that the transformation of diamond into non-diamond carbon and the subsequent dissolution of carbon atoms onto the metal plate are responsible for the material removal during TCP. The two material removal mechanisms compete with each other during polishing. Temperature is the key factor in deciding which mechanism plays the dominant role. It is believed that the conversion of diamond into non-diamond carbon is the primary removal mechanism at high temperatures, whereas the diffusion rate is much faster than phase transformation at lower temperatures. The surrounding environment also affects the MRR and polished surface quality. An MRR greater than 7 µm h\(^{-1}\) was obtained in a vacuum at 950 °C [7]. While the surface roughness of several microns was reduced to 2.7 nm within 8 h of polishing. In contrast to vacuum conditions, polishing in hydrogen environments resulted in a very rough diamond surface and a low MRR of 0.5 µm h\(^{-1}\).

The majority of literature focusing on the TCP of diamonds appeared around the 2000s. In contrast, a minimal number of reports have been published in recent years, mainly because technological limitations hinder the further development of TCP. The complicated vacuum and high-temperature equipment requirements dramatically increase the machining
cost. TCP has limited processing efficiency compared to other techniques, which further undermines its application in the industry. The nonuniformity of the metal plate heating makes polishing thin CVD films incredibly difficult. In short, there is a long way to go before the TCP technique becomes a practical diamond polishing method.

8.2. Laser polishing

LP has attracted significant attention because it is a non-contact polishing technique free from the limitations faced by the other conventional contact polishing methods. Rothschild reported the first ever known LP of diamond in 1986 [44], which was almost 40 years after Einstein [30] theorized the quantum mechanical phenomenon of stimulated emission. Since then, LP of diamonds has developed rapidly. The most widely used laser sources in diamond polishing include excimer lasers [142–145] and Nd-YAG lasers [22, 146, 147]. The former group of lasers mainly operate at a near-UV range from 193 to 351 nm [148], while the later group operates in a visible and near-infrared range from 500 to 1060 nm. The major advantage of excimer lasers is the high optical absorption coefficient in diamonds, providing high energy deposition in a small volume for rapid and total ablation.

Figure 41 shows a schematic of a typical LP of diamond films. The laser source emits a laser beam that passes through an aperture slit and strikes a reflecting mirror. The reflecting mirror focuses the laser beam on the diamond film, which is mounted on a programmable stage, to produce scanning patterns at variable angles of incidence. The laser beam selectively removes surface protrusions due to the difference in the ablation rate at peaks and valleys of the rough diamond surface [21]. Thermal oxidation and evaporation are the dominant material removal mechanisms in LP. The important operating parameters during LP are wavelength (nm), energy density fluence (J cm$^{-2}$), pulse length (ns), repetition rate (Hz), incidence angle (deg.), and spot size. Tokarev et al [143] and Okuchi et al [149] studied the effect of the incident angle of an excimer laser on the polishing rate. They found that the MRR decreases as the incidence angle increases. Pimenov et al [142] investigated the effects of irradiation conditions on the properties of laser-treated diamond film surfaces. They found that the laser beam incidence and pulse duration determine the surface roughness. Ozkan et al [22] used multiple lasers to polish CVD diamond to obtain high MRR and fine polycrystalline diamond films. Wang et al [45] studied the influences of the laser incidence angle and energy fluence on polishing performance. The results show that the polishing rate increased logarithmically with increasing energy fluence while keeping the laser incidence angle and pulse number the same.

As a typical non-contact polishing method, LP has certain advantages, such as pressure-free polishing, which makes it suitable for polishing flat diamond films and CVD diamond films on curved shapes, and drills where traditional contact methods cannot be applied. The reported MRR of LP is several nanometers per minute, much higher than traditional MP. However, the equipment cost for LP is significantly higher than MP. Moreover, it is easy to induce cracks and shock waves due to local overheating during LP of thin CVD films. In general, LP is suitable for coarse polishing to reduce surface roughness from several microns to sub-microns, dramatically shortening the fine finishing time.

9. Discussion and future directions

9.1. Evaluation of polishing techniques

Table 2 shows the critical evaluation of various diamond polishing methods. The polishing techniques were compared based on the following aspects: polishing rate, polished surface quality, polishing temperature, applied load, anisotropic feature, facilities cost, processing cost, and commercialization potential.

MP, TCP, CMP, DFP, and OH radical assisted polishing are conventional contact polishing techniques usually applied to planar surfaces. On the other hand, LP and IBP are non-contact polishing methods, which can process both planar and non-planar surfaces.

It should be noted that MP, DFP, and LP can be conducted at atmospheric conditions without additional heating or environmental control systems. Therefore, the equipment and processing cost of mechanical and DFP is the lowest among the existing polishing techniques. Although IBS, UV irradiation, and PAP can be applied at room temperatures, they require complex systems to create vacuum environments. Theses additional complex systems increase the overall processing cost. CMP should be performed above the melting point of oxidizing reagents, so a heating system must maintain the polishing temperatures. The costs of equipment and processing are moderate because most oxidants have melting points below 300 °C. Furthermore, thermo-chemical or RIE polishing requires a vacuum chamber, high temperatures, and specific gas flows. Both the vacuum chamber and heating systems will inevitably increase the equipment and processing costs.
Table 2. Critical evaluation of the diamond polishing methods.

|                | MP         | TCP       | CMP       | DFP       | LP         | IBS       | RIE       | UV         | PAP        |
|----------------|------------|-----------|-----------|-----------|------------|-----------|-----------|------------|------------|
| Polishing rate | Low (nm h⁻¹) | Moderate  | Moderate  | High      | High       | Moderate  | Moderate  | Low (nm h⁻¹) | Low (µm h⁻¹) |
| Polished surface quality | Smooth | Ultra-smooth | Smooth | Rough | Rough | Smooth | Rough | Ultra-smooth | Ultra-smooth |
| Processing cost | Low | High | Moderate | Low | High | High | High | High | High |
| Polishing temperature | Room | >700 °C | >300 °C | Room | Room | Room | Room | Room | Room |
| Facilities cost | Low | High | Moderate | Low | High | High | High | High | High |
| Anisotropic feature | High | Low | Low | Low | Low | Low | Low | Low | Low |
| Applied load | Moderate | Low | Moderate | High | — | — | — | Low | Low |
| Commercialization potential | High | Low | High | High | Low | Low | Low | High | High |
Of all the polishing techniques, DFP and LP possess the highest MRR of several microns per minute. Thermochemical, chemical-mechanical, reactive ion beam etching, and PAP are second-tier with MRRs of several microns per hour. MP, IBS, and UV irradiation assisted polishing can only remove several nanometers of diamond per hour. The situation is quite different when it comes to polished surface quality. In general, the polishing techniques with the highest MRRs, such as dynamic friction and LP, usually have poor polished surface quality. In such cases, the limiting surface roughness can be tens of nanometers. The surface after reactive beam etching remains rough because of the inhomogeneous etching rates of diamond crystal in different orientations. Furthermore, MP, CMP, and IBS can fabricate a smooth diamond surface with several nanometers surface roughness. Finally, TCP, UV irradiation, and PAP can produce an ultra-smooth diamond surface with sub-nanometer surface roughness.

Before choosing a polishing technique, it is better to know the requirements of a specific application. For example, CVD chemical-resistant coatings do not require high surface quality. LP may be the first choice to process thin featured CVD coatings. However, low surface roughness is required for tribological and optical coatings and electronic and thermal management applications. Thus, the diamond surfaces must be highly polished. According to the above analysis, each polishing technique has its advantages, and it is important to select a proper polishing method after careful consideration and evaluation of all the methods. Considering the balance between the polishing efficiency and quality, LP or DFP can be used for coarse polishing to reduce the surface roughness from microns to tens of nanometers. Mechanical or CMP can further decrease the surface roughness to a few nanometers. If an ultra-smooth and damage-free surface is required in some specific areas, such as chemical growth substrate, IBS and PAP are highly recommended.

9.2. Future directions

The processing efficiency and polished surface quality are the key motivations to develop and apply diamond polishing techniques. This section critically reviews the previous works and future directions of two preceding issues since they determine the application potential of the developed polishing techniques. Since the first scientific investigation on MP of diamond was reported in 1920, various polishing techniques have been developed. The developments and trends of the proposed polishing techniques are illustrated in figure 42.

(a) At the early stage between the 1920s and 1970s, researches focused on optimizing MP. It was found that the processing efficiency largely depends on the crystal orientation and sliding directions. To acquire optimized
According to the current review, the major conclusions are as follows:

(a) MP has a long, rich history and gains attention with every passing day. It was successfully commercialized after a century of systematic scientific research. The optimized machining conditions and easy-to-process crystal orientations were determined and verified by experimental and theoretical simulation analyses. Even during polishing, the atomic evolution process was demonstrated by visual MD simulations. The material removal efficiency and polished surface quality of MP of diamonds should be further improved to maintain its dominant position in commercial production.

(b) As demonstrated by the increasing number of studies, chemical reactions are considered promising solutions in diamond polishing because they have higher MRRs and better surface quality than conventional mechanical cleavage. Thus, various polishing techniques assisted by chemical reactions have been developed in recent decades.

(c) The OH radical assisted CMP is expected to be one of the most promising techniques. Having plenty of OH radical sources at ambient conditions, such as hydrogen peroxide solution, UV irradiation, and plasma beams, ensures low equipment and processing costs. The key advantages of OH radical assisted polishing include ultra-smooth and damage-free diamond surfaces, atomic material removal mechanisms, absence of chemical contamination, and processing efficiency scaled from microns to nanometers per hour.

(d) Although most studies on chemical assisted polishing of diamonds were based on experiments, limited empirical understandings have been gained. Therefore, explanations of some issues are still ambiguous. The key issues are:

1. why chemical assisted polishing could improve or deteriorate the processed surface quality
2. reasons behind the better polishing performance of chemical effects
3. identifying the chemical reactions that can prevent material removal anisotropy and the inherent reasons behind this discrepancy
4. optimization of polishing apparatus designs to achieve better polishing performances based on the selected chemical removal mechanism
5. exploration of analytical or multi-physical numerical models based on the mechanics, chemistry, thermology, and tribology for more profound insights into the basic principle of chemical assisted polishing in the future.

(e) PAP shows extraordinary performance on both processing efficiency and surface quality. Since this method was first introduced in 2018, it is a very new technique, and several issues must be taken into consideration. The future directions of PAP can include optimizing the processing conditions, simplifying the machining equipment, developing various types of plasma sources, identifying the material removal mechanisms, and exploring vacuum-less polishing.

10. Conclusions

According to the current review, the major conclusions are as follows:

- Because of the strong material removal anisotropy of MP, the methods employing chemical reactions to remove carbon atoms have been in key focus. A large number of chemical-assisted polishing techniques were developed between the 1950s and 2000s. The MRR of newly developed methods improved compared to MP. LP, reactive ion beam etching, and DFP improved the MRR to several microns per minute. Although the polished surface quality is unsatisfactory for practical applications, it does not affect the coarse polishing of diamonds. However, polishing methods with multiple superior abilities such as high efficiency and high-quality surface polishing are expected to be developed in the future.

- The number of studies on CMP, RIE, and OH radical assisted polishing significantly increased after 2000, which was due to the increasing production demands and industrial requirements, such as high efficiency and quality polishing, that conventional polishing techniques could not meet. Moreover, the trend of introducing new polishing techniques will likely continue in the future. However, newly developed methods still face some challenges, such as finding a balance between efficiency and quality, simplifying the machining devices, reducing the processing costs.

- Thanks to rapidly developing visual simulation software, the atomic removal mechanism of diamond polishing can be visually analyzed by MD simulations or quantum analyses. So, there is a significant increase in studies exploring the mechanisms of material removal anisotropy in the MP of diamonds. MD simulations are also useful for analyzing the evolution of the chemical bonding process during CMP and OH radical assisted polishing, which contributes to the deep understanding of material removal mechanisms. No doubt, researchers will continue using MD simulations to analyze and visualize the material removal mechanism of other polishing techniques in the near future. However, simulations should be designed to build models consistent with the actual polishing process happening under multiple energy sources.
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Conflict of interest

The authors declare no conflicts of interest.

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