

Chemical Mechanical Polishing of the Apex of Microcrystalline Diamond Coated Hemispheres

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1. Summary

A range of topographies of B-doped polycrystalline diamond coating were produced by chemical mechanical polishing (CMP) of 1 μm thick B-doped (2000 – 4000 ppm) microcrystalline diamond (MCD) coated SiC hemispheres of 3 mm diameter. The CMP process by mechanochemical removal of the oxidised B-doped MCD surface, was performed by use of 70 nm diameter colloidal SiO_2 in deionized water as a polishing slurry, in conjunction with a SUBA X polyurethane-impregnated polyester pad directed onto the apex of the samples, under varying normal forces and sliding speeds. Investigation was carried out on the effectiveness of this CMP process, as well as the effects of normal force and sliding speed on the resulting topography and the tribological interaction taking place. It was found that where interaction between the B-doped MCD coating and polishing pad was inhibited (in this case by further distance from the apex of the hemispherical samples), the main influencing polishing parameter in changing surface topography was sliding speed, with a significantly positive correlation between sliding speed and changes in root mean squared roughness (RMS), root mean squared curvature (Spc) and root mean squared gradient (Sdq). However, where the polishing pad was effectively interacting with the MCD coating in the CMP process (closer to the apex of the samples), normal force was a far more dominating polishing parameter in changing surface topography, with a highly significant positive correlation with changes in RMS, Spc and Sdq. Sliding speed had an insignificant effect on changes in RMS, Spc and Sdq compared to normal force, where the polishing pad was believed to have effective interaction with the MCD coating. For normal force to be an effective influencer of changes in topography during this CMP method, sliding speed must be high enough for the slurry film bearing capacity to not be overcome by the applied normal force, allowing the slurry to enter the pad-MCD interfacial region and therefore for the CMP process to be effective. The CMP process is significantly ineffective where the slurry is predicted to be inhibited from entering the interfacial region. A large number of possible improvements and directions for further investigation, have also been presented within this report.

2. Introduction

2.1. Objectives

The influences on wear of diamond or diamond coatings and other surfaces, where they slide along each other with or without lubrication, is still a widely researched field.¹⁻⁴ As well as providing evidence of the changes due to wear, the topography of diamond at any stage of a surface-surface wear process is a dominating influence on the wear of both the diamond and the surface it is interacting with.^{3, 5, 6} For investigation of how diamond topography influences the wear of the diamond and another surface which it is in sliding contact with, generating a range of topographies was required. A well-known method to produce smoother surfaces of diamond coatings is Chemical Mechanical Polishing (CMP).⁷⁻⁹ The purpose of this project was to perform CMP on Microcrystalline Diamond (MCD) coated hemispheres to produce a variation of diamond coating topographies, as a preparation for following projects to discover the influences of Polycrystalline Diamond (PCD) coating surface topography on the wear between PCD and a substrate. The stages of this work involved setting up a laboratory method for the CMP of MCD films, revealing the influences of different CMP parameters on the surface topography of these films and contributing towards research into their tribological behaviour. Aligning with all stages of this research, contribution of a chapter was also made to a soon-to-be-published literature review.

2.2. ARCNL

This work was performed at the Advanced Research Centre of Nanolithography (ARCNL), which occupies the ground floor and half of the first floor of the Matrix building within the Science Park of Amsterdam. ARCNL has close ties with its neighbours both AMOLF research institute and the University of Amsterdam (UvA) (Universiteit van Amsterdam), as well as the more geographically distant Free University of Amsterdam (VU) (Vrije Universiteit Amsterdam), though collaboration with other universities worldwide is frequent. Funded partially by the Dutch Research Council (NWO) (Nederlandse organisatie voor Wetenschappelijk Onderzoek), ARCNL is a semi-publicly funded research company, with the mission to investigate fields of physics with the highest significance and relevance in nanolithography technologies. The company is also relatively young having started in 2014, though it employs just under 100

researchers, the majority of which are PhD students and postdoctoral fellows supervised by assistant, associate and full professors. As would be predicted from the name, ARCNL focuses on the various influences on the products of nanolithography applications. As there are many influential factors, more continue to be discovered and greater depth of some are discovered, ARCNL continues to grow, the company currently has 3 main departments; source, metrology, and materials, divided into a total of 13 groups, including 2 having started up in September this year. Each group focuses on a particular field, such as plasma theory and modelling or high-harmonic generation and extreme ultraviolet science. The groups are approximately equal in their number of researchers and many inter-group and inter-departmental collaborative projects are carried out, generating a large number of publications (37 so far this year) and PhD theses (10 predicted within 2021). The work outlined in this report was performed from within the Contact Dynamics group of the materials department, which is focussed on how friction and wear at different scales, interface topography, and friction and wear variations over time, influences high-precision positioning under different conditions. The group is led by Prof. Steve Franklin and Dr Bart Weber, and currently consists of 2 post-doctoral researchers, 4 PhD students and 4 master student interns, all of which contributing towards a supportive team.

2.3. Diamond

Diamond is one of the hardest (Vicker's hardness up to 100 GPa) and chemically inert materials known, also with high thermal conductivity ($20 \text{ W cm}^{-1} \text{ K}^{-1}$ at room temperature), high elastic modulus ($\sim 1200 \text{ GPa}$) and low coefficient of friction (COF).¹⁰⁻¹⁸ Diamond as a single "piece", known as Single Crystalline Diamond (SCD) is formed of a uniform lattice of carbon bonded through single covalent bonds in tetrahedral arrangement (due to sp^3 hybridisation), forming a unit cell that is face-centred cubic with two-atomic basis, shown in Figure 1a.¹⁹⁻²² This uniform arrangement results in "hard" and "soft" directions for carbon atom removal by cleavage, where hard directions require greater effective energy in that direction for carbon removal to be successful, and the type of carbon removal is more likely to be as fracturing or chipping, producing newly formed surface that contain pyramidal features, the hard and soft directions are displayed according to the respective planes in Table 1.¹⁹⁻²⁴ However, cleavage in the soft directions requires less applied energy for carbon removal and is more likely to produce newly

formed surfaces that are smooth.¹⁹⁻²³ PCD, often used for material surface coatings, is a combination of a large number of diamond crystal grains, grown on a surface in significantly random orientation, with the most common forms named according to the relative diamond grain sizes; MCD (crystal size $\geq 1 \mu\text{m}$), Submicrocrystalline Diamond (SMCD, $200 \text{ nm} \leq \text{crystal size} < 1 \mu\text{m}$), Nanocrystalline Diamond (NCD, $10 \text{ nm} \leq \text{crystal size} < 200 \text{ nm}$) and Ultra-Nanocrystalline Diamond (UNCD, crystal size $< 10 \text{ nm}$) (Figure 1b).^{14, 25} By a relatively cheap and effective method, PCD is usually “grown” onto a substrate surface as a coating by chemical vapour deposition (CVD) where it can provide significant benefit in applications such as thermal management, surface acoustic wave devices, and tribological tools (e.g. extending use duration of micro-drills).^{9, 14, 25, 26} The extent to which PCD can provide benefit within these fields is largely determined by PCD film thickness, adhesion to the substrate beneath the PCD coating and topography of the PCD coating.^{9, 14, 25} PCD coating thickness influences the edge radius of cutting tools, life of diamond-coatings and the associated substrates, and coating delamination, with the latter two also being heavily influenced by effectiveness of the PCD adhesion to the surface beneath.²⁷⁻³⁰ The topography of PCD coatings, mainly the roughness, has demonstrated to show large influence on wear rate on a substrate as well as the friction and adhesion with other surfaces, though further ability to characterize the topography and understand its influence on wear is still being understood, therefore making the work carried out within this report highly relevant for the field of tribology currently.^{6, 31, 32}

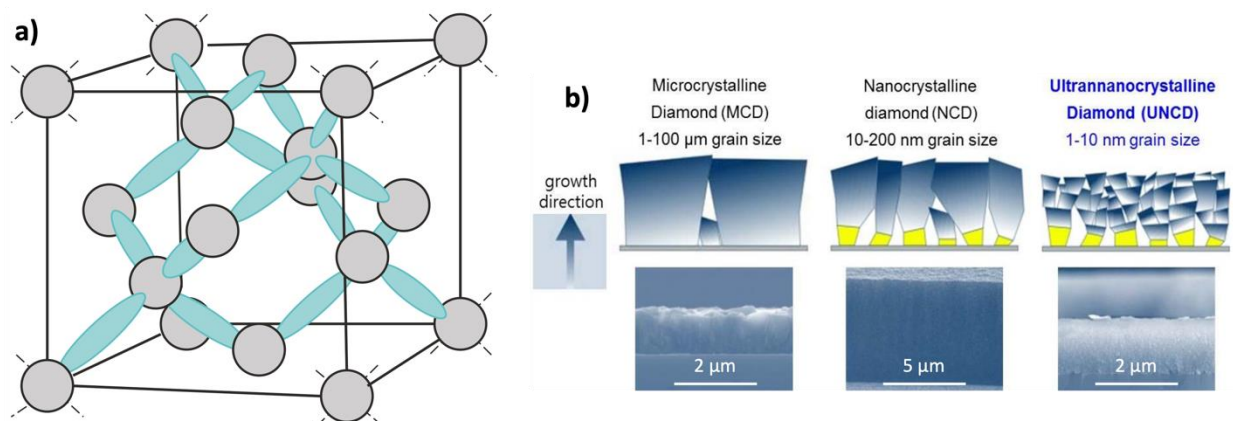
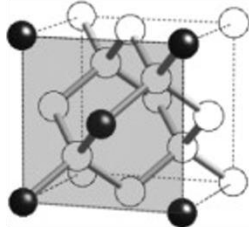
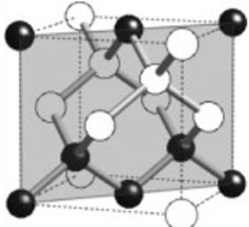
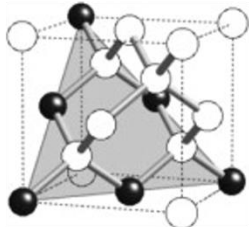
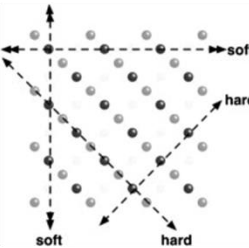
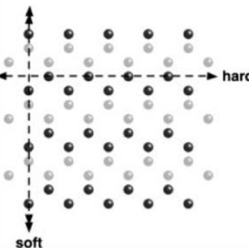
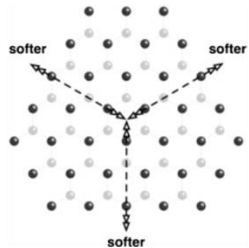


Figure 1: Diagram of the unit cell of diamond (face-centered cubic with two atomic basis) (a) and schematic and cross-sections of the 3 most common forms of polycrystalline diamond; microcrystalline diamond (left), nanocrystalline diamond (middle) and ultra-nanocrystalline diamond (right) (b).¹⁹

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Table 1: Table demonstrating the “hard” and “soft” polishing directions for diamond according to the C-C covalent bond angles and interatomic distances associated with different planes of the diamond unit cell.²⁴

Crystallographic	Cubic	Dodecahedral	Octahedral
Polisher	Four-point	Two-point	Three-point
Plane group	{100}	{110}	{111}
Lattice views			
Plane views identifying hard and soft polishing directions			

2.4. Chemical Mechanical Polishing

CMP is applied to hard materials (such as diamond, sapphire and silicon carbide) to produce smooth surfaces with minimal sub-surface damage, as the name suggests the process is effectively carried out by a balance of chemical reaction and mechanical action by abrasive.^{11, 18, 25, 33} As is often when assessing the tribology of two surfaces, many mechanisms are in effect simultaneously at any point in the interaction, and it is the balance of the mechanisms employed which can be altered, by varying the applied method for tribological interaction and the relative effective parameters for each. For the purpose of CMP of diamond three effective method types can be performed; mechanical removal of the chemically oxygenated surface by use of a non-oxide hard abrasive such as diamond or boron carbide in an oxygenating water-based environment, mechanochemical removal of the chemically oxygenated surface by use of an oxide abrasive such as silica, alumina or ceria in an oxygenating water-based environment, and removal of mechanically deformed surface such as using a metal plate at high temperatures for carbon atom diffusion into the plate or chemical reaction of carbon atoms that have been removed or partially-removed mechanically from the surface to produce and

evaporate as CO₂ gas.^{8, 11, 15, 34-37} When performing CMP of diamond by either mechanical or mechanochemical removal of the chemically oxygenated surface, the oxygenation of the surface carbon atoms effectively lowers the energy requirement to break the C-C single covalent bonds between the surface carbon atoms and the carbon atoms beneath the surface layer, enabling mechanical action by abrasive and/or polishing pad/plate to break the C-C bonds and remove the products.³⁸⁻⁴¹ Some of the potential mechanisms that can take place during CMP of diamond include graphitization (conversion of carbon atoms into graphite form), conversion of carbon atoms into diamond-like-carbon (DLC, a mixture of carbon atoms in sp³ and sp² hybridizations), micro-chipping (chipping away of micro-“chunks” of the PCD structure) and removal by diffusion, evaporation or abrasive action of atomic or nano-sized surface area which has been oxygenated, though as mentioned before, it is through a complex combination of these mechanisms (and potentially others) that each CMP method is employed.^{10, 11, 15, 16, 18, 42, 43} One of the most frequent, recently-used setups for performing CMP on diamond is shown in Figure 4, where the diamond substrate is held in place by a rotating platform with normal force applied (labelled “head pressure”) into the diamond and rotating polishing pad, polishing slurry (water-based, consisting of abrasive particles and oxidant) is constantly distributed onto the polishing pad to be carried by the pad rotation into the interfacial region between pad and diamond, a conditioner is applied to the polishing pad to remove polishing products embedded in the pad and “refresh” the pad topography.^{42, 44-46} A balance of the parameters of CMP, such as the applied normal force, flow rate, slurry composition (pH, oxidant type and concentration, abrasive type and size etc.), pad hardness, pad topography, and sliding speed of polishing pad & substrate, has effects on the balance of mechanisms and therefore the COF, Material Removal Rate (MRR) and change in surface topography are all directly affected.^{10, 11, 18, 42, 43}

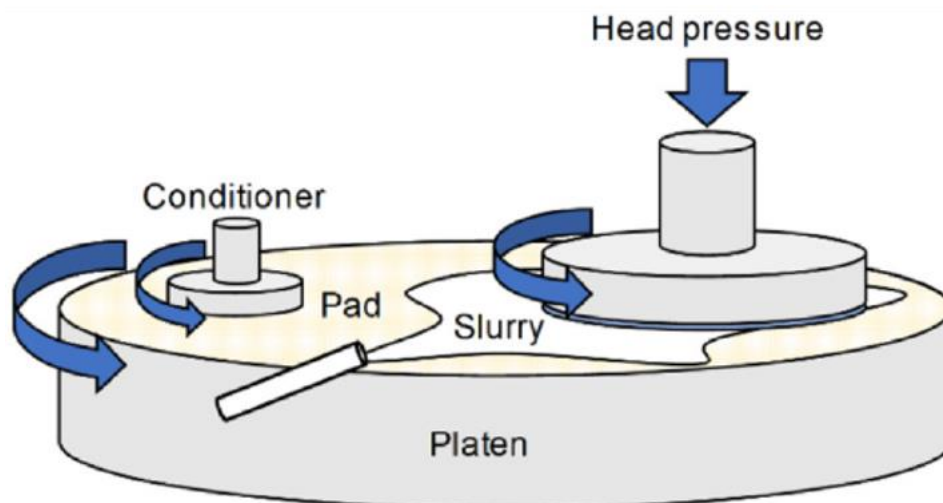


Figure 2: Diagram of a current, commonly used setup for performing chemical mechanical polishing of diamond.

2.5. Relevant Influences on CMP of Diamond

For the purpose of these experiments, the method of silica-abrasive mechanochemical removal of chemically oxygenated diamond surface was applied, as this method has been revealed within literature to demonstrate high MRR and change in surface topography with minimal subsurface damage.^{25, 35, 47} When applying this method of CMP of diamond, sliding speed of the polishing pad has a strong positive influence on slurry flow into the interfacial region and therefore also a strong positive influence on rate of contact between slurry components -such as the abrasive- and the diamond surface.^{42, 43, 48, 49} Increasing normal force leads to an increased rate of interaction between abrasive and diamond substrate, as well as the probability for chemical bonds to form between the two, resulting in increase of friction force, however increasing sliding speed leads to a decrease in friction force and COF due to increased bearing capacity of the liquid film (introduced by increased flow of slurry into the interfacial region), reducing the effective normal force acting directly on the substrate from the abrasive.^{7, 50-52} At the atomic level, increasing normal force increases the rates of decomposition of oxidants & H₂O and the subsequent adsorption of the products onto the diamond surface, however flow rate must be high enough to provide availability of oxidants & H₂O for this process.^{7, 45} On the larger scale, where slurry flow rate into the interfacial region is decreased and/or normal force is increased to certain extents during CMP, the process becomes more mechanically-dominated between the polishing pad and diamond substrate as opposed to

increasing slurry flow rate into the interfacial region and/or decreasing normal force which leads to greater extent of chemical reaction involving the slurry components, including abrasives, this also decreases subsurface damage of the substrate.^{7, 43, 48, 50, 53} CMP of PCD is reported to have been performed many times by use of a much softer polyester/polyurethane polishing pad with colloidal silica abrasive in water to decrease surface roughness and increase MRR.^{8, 9, 15, 25, 54} The “atom-by-atom” mechanism that allows this method to be successful has been proposed experimentally and proven computationally; first oxygenation of the diamond surface carbon atoms takes place by water (and oxidant if present, which accelerates the process), silicon then bonds to the oxygen of the $C_{\text{surface}}\text{-O}$ bond formed and neighbouring Si, and O atoms of the silica can also bond to a nearby C_{surface} atom, finally sliding action from the polishing pad acts upon the abrasive and there is significant probability for the surface carbon atom to be pulled out of the surface.^{8, 9, 15, 25} This successful atom removal is proposed to be due to the polar nature of the Si-O bonds in the silica abrasive, which increases strength of the Si-C and O-C bonds, whilst this polarization also influences and decreases bond strength between the newly bonded carbon atom and neighbouring carbon atoms, therefore introducing probability for this pulling action to break the $C_{\text{surface}}\text{-}C_{\text{neighbour}}$ bonds resulting in carbon atom removal.^{7, 9, 15} Investigation of this mechanism by Peguiron et al. revealed that the key point for successful carbon atom removal by this mechanism, is that the local electronic environment of the terminating C-C covalent bonds between the carbon zig-zag chains and bulk diamond when the aromaticity is retained, result in these bonds being susceptible to this polarizing activation and subsequent carbon atom removal (Figure 3).¹⁵

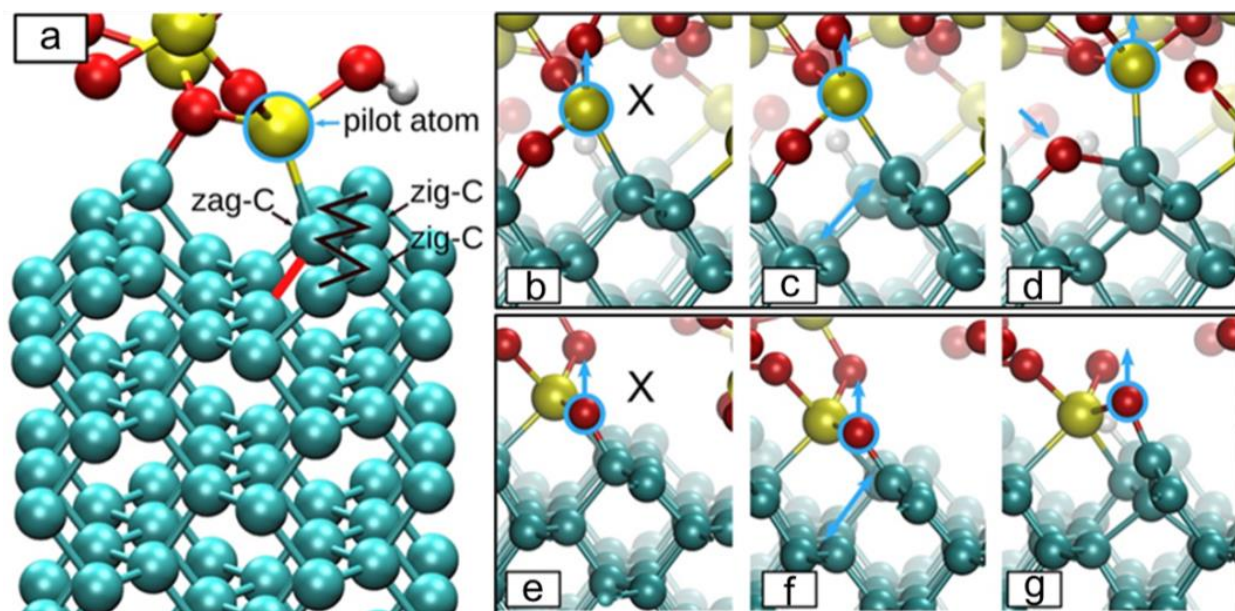


Figure 3: Density-functional tight bonding molecular dynamics simulation illustrating the zig-zag carbon chain of a diamond surface susceptible to carbon atom removal via silica (a), and the C-C single covalent bond breaking process of a carbon atom within said zig-zag chain with the carbon atom single covalently bonded to silicon (b-d) or oxygen (e-g) of silica.¹⁵

2.6. Brief of Report

In this set of experiments, the apex of B-doped MCD coated SiC hemispheres of 3 mm diameter were prepared for investigations in wear by producing changes in topography of the coatings by CMP. For the purpose of CMP, a polishing slurry of SiO₂ in deionized (DI) water was used with a “soft” polyurethane/polyester polishing pad to ensure the dominating factor of the CMP mechanisms was chemical reaction between slurry and MCD surface. To produce a topographical range by using polishing parameters that could be repeated for future sample preparation and partially-investigate the acting CMP process, both sliding speed and normal force were varied. The setup used for this CMP is displayed in Figure 4a. The topography of the MCD coating was analysed by Scanning Electron Microscopy (SEM), optical focus variation profilometry and Atomic Force Microscopy (AFM). The quantitative results obtained by optical focus variation profilometry and AFM were used to produce Root Mean Squared (RMS) roughness values (equation and illustration in Figure 4b) to demonstrate the average height difference across the coating surface (ignoring spherical background), these values have been used to great effect in demonstrating changes in topography due to CMP.^{8, 13, 33} However, to investigate the topographical changes in more depth, the quantitative results obtained were

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also used to produce Arithmetic Mean Peak Curvature (Spc) (equation and illustration in Figure 4c) and root mean squared gradient (Sdq) values (equation and examples in Figure 4d) in the case of optical focus variation profilometry. In the case of the AFM results, just Sdq values were calculated due to limitations in the AFM results processing software.

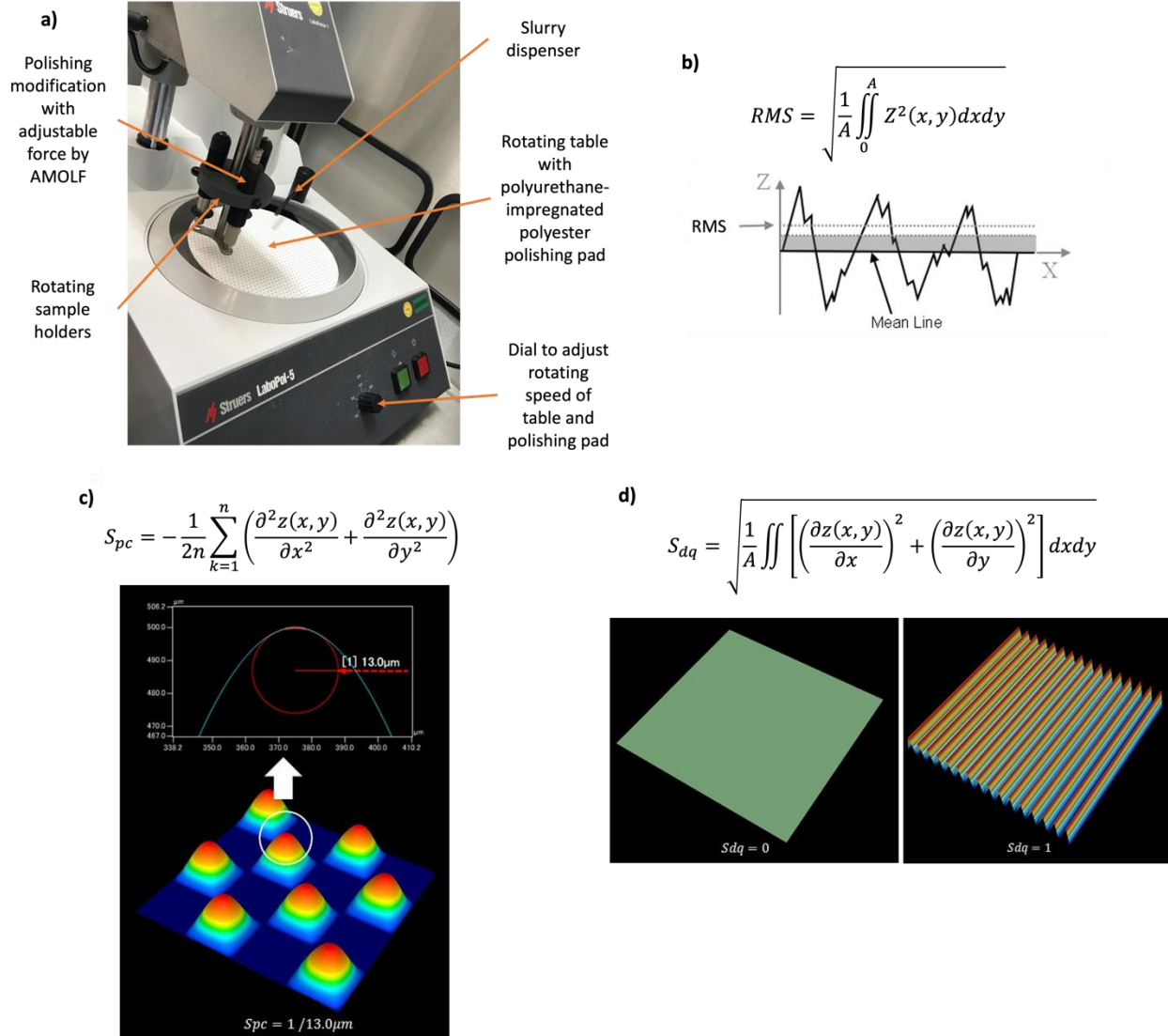


Figure 4: Photo diagram of the setup used for this report to perform chemical polishing on B-doped (2000 – 4000 ppm) microcrystalline diamond coated SiC hemispheres (a), the equation and an illustration to demonstrate root mean squared (RMS) roughness (b) the equation and an illustration to demonstrate mean peak curvature (Spc) (c) and the equation of root mean squared gradient (sdq) and an example of surface with $sdq = 0$ (flat surface) (left) and $sdq = 1$ (45° gradient segments) (right) (d).^{55, 56}

3. Experimental

3.1. Design

For producing a topography range of diamond coating on hemispheres with minimal damage by CMP, a more chemical-based method was chosen, with materials of much lower comparative hardness compared to the diamond coating. The method chosen was therefore to use polar silica abrasives known to react with the diamond surface to perform CMP, rather than hard abrasives known to push the balance of acting mechanisms to those that cause subsurface damage. Other polar abrasives such as alumina and ceria could also have been used as effective abrasives in this case, though literature appeared to show use of silica exhibited greater MRR and change in surface roughness compared to these other two abrasives, also the chemical reaction between silica and diamond could have proved interesting to other projects at ARCNL.^{25, 39} A much softer polishing pad was also decided upon to ensure polishing was performed as much as possible by the silica abrasive and with minimal surface-surface wear between the diamond coating and a polishing pad of more similar hardness. To accelerate the silica abrasive CMP process oxidants are usually used, however, for the purpose of health and safety purchasing an oxidant was restricted unless deemed absolutely necessary, therefore the silica abrasive within water was the resulting slurry used, with water being the mild oxidiser as well as the local environment of the interfacial region during CMP.^{8, 18, 40} Almost all the relevant diamond CMP literature referred to in the introduction involves polishing for several hours, with analyses at specific time intervals, this was considered unnecessarily time consuming for the goals of this research as the literature usually is outlining how to get to the smoothest surface possible from a sample, whereas the purpose included development of a specific preparation method for a large series of samples, with higher speed of preparation being a significantly beneficial quality, time was kept constant at 10 minutes for the CMP experiments outlined in this report. As detailed in the introduction, the balance of sliding speed and applied normal force appeared to affect the mechanism, MRR and change in surface topography of diamond coatings polished using oxidant and/or silica in DI water. With restrictions in time and use of a strong oxidant, though the ability to adjust sliding speed on the polishing machine

already (Figure 4a), adjusting normal force in combination with sliding speed aligned well with the goals and restrictions of this project.

Several methods were chosen for analysis of the diamond surface after polishing to ensure a complete overview of the chemical and topographical changes produced from CMP. AFM was performed due to the high sensitivity of the AFM equipment, producing image quality close to the nanometre scale with quantitative results, also considered effective in revealing changes in topography of the individual diamond grains. The limitations of AFM were in the maximum size of the area that could be measured (90 μm x 90 μm), as well as the minimum scan time per line within each image (0.1 Hz) resulting in image quality loss as scan area is increased. Optical profilometry was used to demonstrate the topography change in larger area sizes (702 μm x 526 μm and 283 μm x 212 μm) and produce representable real colour images by laser and optical as well as obtain quantitative results. To enable easier identification of the area of polishing to analyse under the microscope of the AFM, and examine the surface topography in ranges outside of those obtained by profilometry and AFM, as well as producing good quality images in shorter time frames than AFM, SEM was used. Although SEM could not produce quantitative data from the images obtained, it was considered useful to view the topography by SEM images to obtain a more complete assessment. EDX was also added to the analyses techniques to observe any polishing reactants and products not removed from the surface to ensure that the cleaning method was effective and that the topography variation observed was of diamond alone.

3.2. Laboratory Setup

A Struers LaboPol-5 polishing machine with Struers LaboForce-1 sample holder rotating platform was provided though heavily damaged (Appendix A1), the damage was assessed and new parts ordered accordingly (new tap, splashguard, and casing with polishing bowl and output tube) and fixed to the polishing machine before electrical safety testing was carried out, the fixed polishing machine is displayed in Figure 4a. To produce an effective CMP method using the polishing machine, an effective combination of slurry and equipment - including relevant safety precautions - was designed and all components were purchased and implemented, along with a Standard Operating Procedure (SOP) (Appendix B). A modification

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was designed and produced by the AMOLF research institute for adjusting normal force applied onto the diamond coated hemisphere samples, using a spring inside the modification and detachable hemisphere holders for each sample, this modification is displayed in Appendix C. The hemisphere holders allowed exposure of the apex area of each hemisphere sample to 2.6 mm diameter whilst restricting movement of the hemisphere during polishing or subsequent analyses. The spring force exertion of the modification according to compression distance was determined using an Instron 3400 Series with an Instron Static Loading Cell 2530 Series with ± 10 N capacity, the results of which are displayed in Appendix A2. A peristaltic pump (Verderflex Peristaltic Electric Operated Positive Displacement Pump 0.24 L/min, 12 V) was used to constantly feed the stock slurry mixture onto the polishing pad (0.18 L /min (provided with 9 V power feed)) (Appendix A3a). A SUBA X Perf II 08 polyurethane-impregnated polyester polishing pad was used due to the much lower hardness (Shore D0 hardness 44) compared to diamond, high efficiency in slurry transport (due to perforations within the pad) and large-use in recent literature demonstrating successful diamond CMP using similar slurry components (Appendix A3b).

3.3. Chemical Mechanical Polishing

Boron-doped (B-doped) (2000 – 4000 ppm) MCD coated (1 μ m thickness) samples were prepared by the company Faunhofer, by 1-stage seeding and chemical vapour deposition (CVD) onto silicon carbide hemispheres (3 mm diameter). Slurry production and CMP were performed in an open laboratory at Standard Ambient Temperature and Pressure (SATP). Eminess Ultra-Sol™ S27 (SiO₂ colloidal spheres (70 nm diameter) within deionized (DI) water (50 % weight/volume) (pH 9)) (500 $\pm$ 10 mL) was diluted with DI water (1000 $\pm$ 10 mL) and subject to stirring (90 sec, 400 rpm) by magnetic stirrer bar to produce a colourless, translucent mixture (1500 $\pm$ 20 mL). The resulting mixture was transferred to a 10 L container and the process of producing the mixture was repeated 3 more times to produce the stock slurry mixture (6000 $\pm$ 80 mL, 17 % SiO₂ weight/volume, pH 9). Chemical mechanical polishing (CMP) was performed for 10 minutes on each of the B-doped MCD coated samples using the polishing setup. The applied normal force exerted by the polishing modification onto the samples against the slurry and polishing pad was varied across three pairs of samples (0.62 $\pm$ 0.21 N, 3.1 $\pm$ 0.2 N and 5.2 $\pm$

0.2 N), and the rotational speed of the polishing pad applied against the samples was varied within each pair (50 rpm and 200 rpm). Counter rotation was also carried out based around the centre of the LaboForce-1 sample holder (8 rpm, 0.022 ± 0.001 m/s), the position of the centre of the sample holders on the polishing pad could only be set by-eye and the sample holders tended to drift away from the centre of the polishing pad during CMP due to the normal force and sliding applied before being pushed back by-hand. The mean average of the range of possible distances between the centre of polishing pad and the centre of the LaboForce-1 sample holder was used to produce the sliding speeds, and the range was used to produce the error of sliding speeds relative to the centre of the LaboForce-1 sample holder (0.30 ± 0.09 m/s and 1.22 ± 0.38 m/s).

3.4. Post-Polish Cleaning

Following CMP, the samples were cleaned by subjecting them to 5 minutes ultrasonic cleaning in ethanol within a HBM digital heated ultrasonic cleaner (HBM GL serie 2.5 L Ultrasoon reiniger) (25 °C, 20 kHz). Without removing the samples from the ethanol, the samples were then rubbed using a cotton bud sliding in the same direction for 2 minutes. After sliding using a cotton bud, the samples remained in the ethanol for another 5 minutes ultrasonic cleaning, before being transferred for a final 5 minutes ultrasonic cleaning in DI water to remove the ethanol. Samples were left to dry in air in an open laboratory at SATP for 2 hours before being transferred to a closed container and stored in a nitrogen gas cabinet.

3.5. Analysis

Optical profilometry and AFM were both performed in an open room at SATP. The polished samples and an unpolished sample were analysed centred around the apex by optical focus variation profilometry, using a laser-scanning confocal microscope (Keyence VK-X1000), at 20 x magnification over an area of $702 \mu\text{m} \times 526 \mu\text{m}$ (resolution $686 \text{ nm} / \text{pixel}$ and $659 \text{ nm} / \text{pixel}$ respectively), and also at 50 x magnification over an area of $283 \mu\text{m} \times 212 \mu\text{m}$ (resolution $138 \text{ nm} / \text{pixel}$ along both axes). All optical profilometry analyses were centred around the apex (identified as the highest point by the laser image), the images produced are in Appendix A4 and Appendix A5. The profilometry images were processed and analysed using Keyence MultiFile Analyzer, the results of which are displayed in Figure 8 and Figure 9. Three unpolished

samples were analysed at the apex of the hemisphere by AFM using a Bruker Dimension ICON with ScanAsyst by 'Tapping Mode in Air' with a Bruker RTESPA-300-30 AFM probe, (30 ± 4.5 nm tip radius made of antimony-(n)-doped silicon) at resolution 2048 pixels x 2048 pixels in $90 \mu\text{m}$ x $90 \mu\text{m}$ areas, an optical image was taken during each of these AFM analyses, the optical and AFM images are displayed in Appendix A6. The apex area of each hemisphere sample was identified as the first section to become focused under the Bruker Dimension ICON optical microscope, when the AFM piezo was lowered down towards each sample, with the apex directed upwards. The $90 \mu\text{m}$ x $90 \mu\text{m}$ AFM micrographs were processed using Gwyddion 2.58 (64 bit) to remove the spherical background, correct horizontal scarring, and adjust the false colour mapping range representing height to a colour range that appeared easier to assess (colour range named 'Gwyddion.net'). It was discovered that representable results of greater accuracy could be obtained by AFM micrographs covering a smaller area (due to limitations by a minimum scan rate of pixel line per sample area), therefore each polished sample and three unpolished samples were analyzed multiple times within the apex area of the hemisphere ($\sim 100 \mu\text{m}$ x $100 \mu\text{m}$) at resolution of 512 pixels x 512 pixels in $5 \mu\text{m}$ x $5 \mu\text{m}$ areas. The $5 \mu\text{m}$ x $5 \mu\text{m}$ AFM micrographs were processed by the same means as the $90 \mu\text{m}$ x $90 \mu\text{m}$ AFM micrographs. Samples images were also obtained by FEI Verios 460 Scanning Electron Microscope, these are displayed in Figure 5, Figure 6 and Appendix A7. Energy Dispersive X-ray (EDX) mapping analysis was performed using the same SEM equipment and an Oxford X-Max 80 mm² Energy Dispersive Spectrometer detector, the resulting images are displayed in Figure 7, Appendices A8 – A12.

4. Results and Discussion

The MCD coatings of the unpolished samples were observed to show significant holes and markings, as shown within the AFM micrographs and optical images (Appendix A6) and optical profilometry image (Appendix A4). These holes were discovered to be produced during the CVD process due to incomplete seeding and PCD growth by the supplier, as the hemispherical shape of the samples made CVD preparation and process difficult.

4.1. SEM results

Three techniques were applied together during SEM analysis to locate the area of most significant polishing within the apex area; the first was to identify a noticeable change in how the surface looks on a larger scale compared to the unpolished sample, once one or more areas had been identified by this method, the areas were subject to greater magnification to observe any significant changes of the diamond grains, finally it was discovered by SEM and EDX mapping images that colloidal silica was still present in the holes of the MCD coating (Appendices A7 – A9), these silica particles were not observed in areas of seemingly unchanged topography, so it was taken that the presence of colloidal silica was also evidence of the most significant polishing taking place in that area. The ability to observe colloidal silica within the holes of the MCD surface and not on the MCD surface itself was taken to be evidence that the cleaning had been effective in removing silica from the MCD surface, though not from the holes in the MCD coating. Larger scale SEM images were taken to include the whole area of most significant polishing for each polished sample and of the general surface area for the unpolished sample, as shown in Figure 5. SEM images were also taken within the area of most significant polishing of each polished sample, as well as the MCD surface of an unpolished sample, with image size ($5.18\text{ }\mu\text{m} \times 3.72\text{ }\mu\text{m}$) similar to the AFM micrographs ($5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$), for potential effective comparison, as shown in Figure 6.

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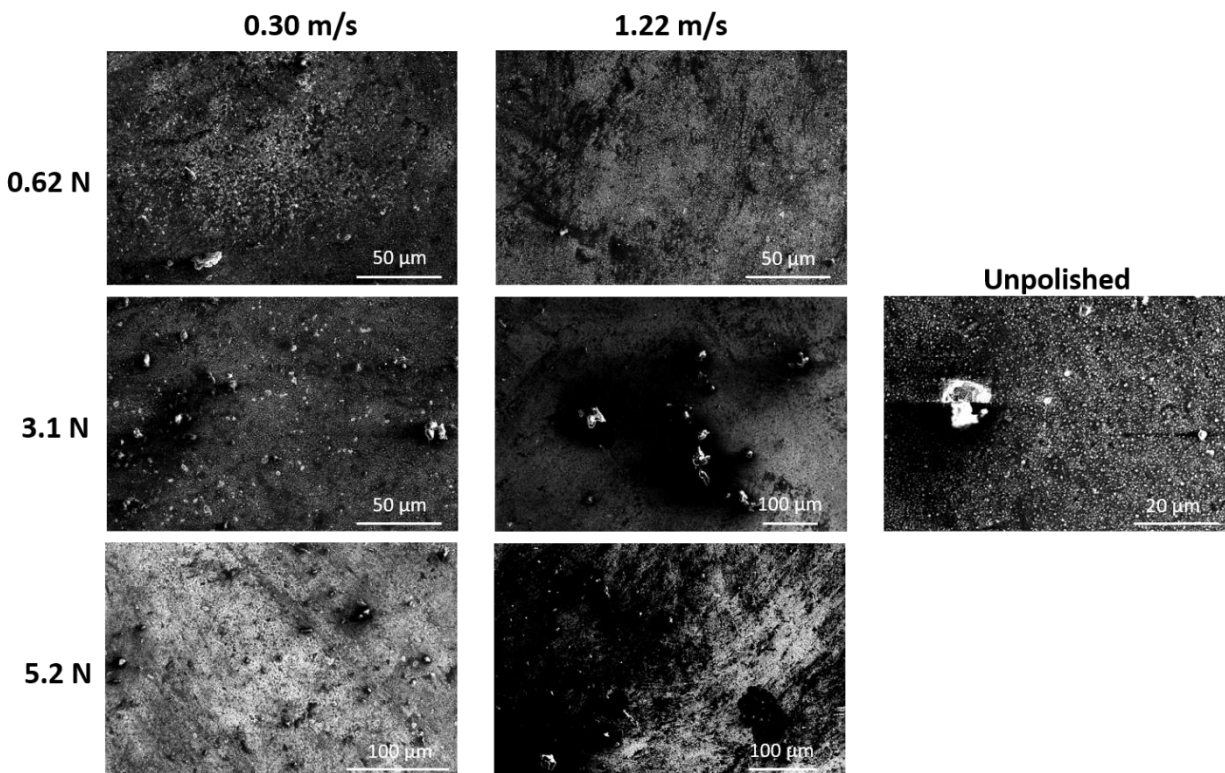


Figure 5: Scanning electron microscopy images showing the largest image of the identified area of significant chemical mechanical polishing of B-doped (2000 – 4000 ppm) microcrystalline diamond coated SiC hemispheres (3 mm diameter) when performed under normal forces of 0.62 ± 0.21 N (top row), 3.1 ± 0.2 N (middle row of left and middle columns) and 5.2 ± 0.2 N (bottom row) and average sliding speeds of 0.30 ± 0.09 m/s (left column) and 1.22 ± 0.38 m/s (middle column), as well as the apex of an unpolished sample (right). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. SEM images were obtained by FEI Verios 460 SEM.

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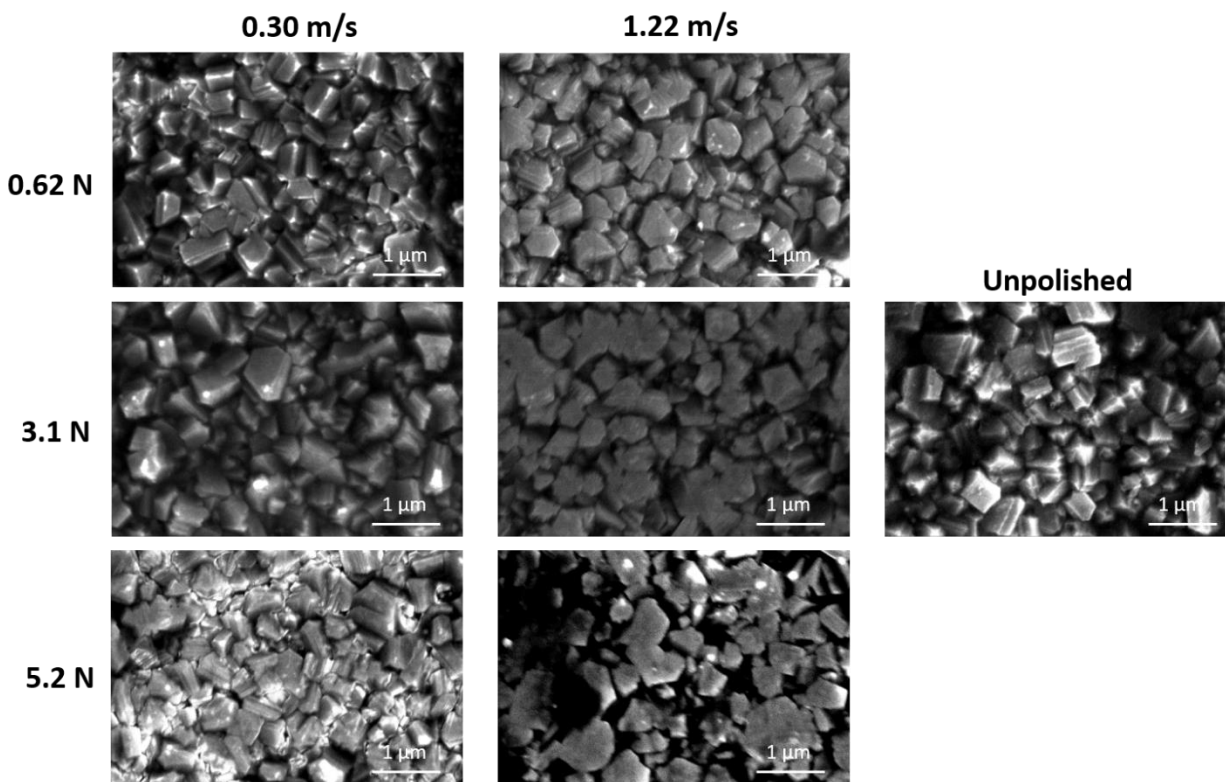


Figure 6: Scanning electron microscopy images ($5.18 \mu\text{m} \times 3.72 \mu\text{m}$) within the identified area of significant chemical mechanical polishing of B-doped (2000 – 4000 ppm) microcrystalline diamond coated SiC hemispheres (3 mm diameter) when performed under normal forces of $0.62 \pm 0.21 \text{ N}$ (top row), $3.1 \pm 0.2 \text{ N}$ (middle row of left and middle columns) and $5.2 \pm 0.2 \text{ N}$ (bottom row) and average sliding speeds of $0.30 \pm 0.09 \text{ m/s}$ (left column) and $1.22 \pm 0.38 \text{ m/s}$ (middle column), as well as the apex of an unpolished sample (right). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. SEM images were obtained by FEI Verios 460 SEM. These images were taken in a manner to avoid larger particles not part of the microcrystalline diamond surface and holes produced because of issues during the microcrystalline diamond coating growth onto the SiC hemispheres.

The lower magnification SEM images of Figure 5 show that particles not intrinsically part of the MCD coating are present on unpolished and polished samples, these particles have not been removed by the cleaning process and appear to build up electronic charge which affected SEM image quality, producing high contrast with darker areas around these brighter particles. The charging of these particles was taken to be further evidence that these were not intrinsic parts of the MCD coating, as the ability to ground the charge through the B-doped crystalline structure was significantly limited. The amount of these particles observed (including observation by identifying areas of high contrast) on the polished samples appeared to be highest and second highest in the samples polished at the highest normal force ($5.2 \pm 0.2 \text{ N}$) and medium normal force ($3.1 \pm 0.2 \text{ N}$) with the highest sliding speed ($1.22 \pm 0.38 \text{ m/s}$)

respectively, the third highest appeared to be in the sample polished at the medium normal force with lowest sliding speed (0.30 ± 0.09 m/s). The remaining polished and unpolished samples appeared too similar in their amount of these particles present to make distinct comparative observations. This was taken as evidence that the amount of these particles observed, correlated moderately and positively with both normal force and sliding speed, excluding the case of where the highest normal force and lowest sliding speed were applied in combination. Apparent scratching was also observed in the SEM images of the polished samples within Figure 5, this scratching appeared to be present to the highest extent in the sample polished at highest normal force with highest sliding speed. The samples polished at the medium and lowest normal force (0.62 ± 0.21 N) with highest sliding speed and highest normal force with lowest sliding speed appeared significantly scratched to very similar extents, the remaining polished and unpolished samples appeared absent of significant scratching. The observations of this scratching was taken to show a weak and positive correlation with the amount of these particles produced, as well as the weak and positive correlation with both normal force and sliding speed applied during CMP.

The SEM images displayed in Figure 6 appeared to show the most significant differences in topography within the samples polished at the highest (5.2 ± 0.2 N) and medium (3.1 ± 0.2 N) normal forces with highest sliding speed (1.22 ± 0.38 m/s). The changes in topography appeared to reveal a general loss of crystal peaks and edges, and therefore a general “flattening” of the MCD surface, this was all considered highly significant evidence of effective polishing. It was considered by observation of the SEM images in Figure 6, that the samples polished at the highest sliding speed had been polished to greater effectiveness than the samples polished at the lowest sliding speed (0.30 ± 0.09 m/s). A trend was taken to be apparent within the samples polished at the highest sliding speed, where increasing normal force applied correlated significantly and positively with increased effectiveness of polishing. Within the samples polished at the lowest sliding speed, although they appear mainly similar, slight increased effectiveness of polishing was observed in the ascending sample order as follows: highest normal force, lowest normal force (0.62 ± 0.21 N), medium normal force. This was taken as significant evidence that sliding speed and normal force showed a strong and

positive correlation with effectiveness of the polishing, excluding the sample polished with the combination of highest normal force and lowest sliding speed.

4.2. EDX results

The technique used in '4.1. SEM results' to establish the areas of most significant polishing was used to identify areas for effectively representative EDX mapping images, these EDX maps were used to identify differences in concentrations of silicon, oxygen and carbon and are shown in Appendices A9 – A11 inclusive. It was observed from these maps that particles not intrinsically part of the MCD coating structure (also observed in 4.1. SEM results) were highly oxygenated in comparison to the rest of the MCD surface in each of the polished and unpolished samples. EDX maps were also taken of the same areas with the carbon mapping absent (Figure 7, Appendix A8 and Appendix A12). Comparison of the EDX maps without carbon signal against the maps including carbon signal revealed that the MCD surface of polished and unpolished samples showed a large absence of both silicon and oxygen, as such it was confirmed that the MCD coatings had been polished, cleaned effectively and analysed without removing the MCD coating and exposing the silicon carbide surface. Larger scale EDX maps of each sample, showing the identified area of most significant polishing, as well as the surrounding area are shown in Figure 7.

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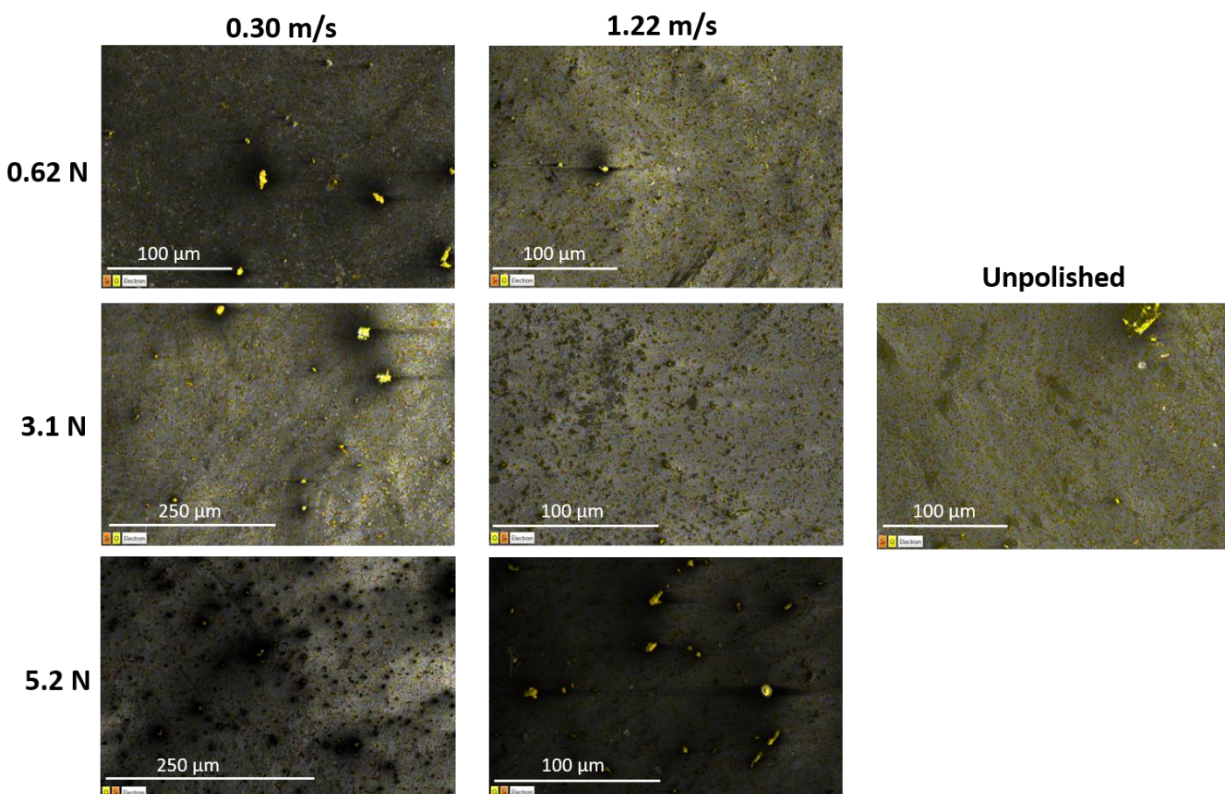


Figure 7: Energy dispersive x-ray overlaid oxygen (yellow) and silicon (orange) maps of the identified area of significant chemical mechanical polishing of B-doped (2000 – 4000 ppm) microcrystalline diamond coated SiC hemispheres (3 mm diameter) when performed under normal forces of 0.62 ± 0.21 N (top row), 3.1 ± 0.2 N (middle row of left and middle columns) and 5.2 ± 0.2 N (bottom row) and average sliding speeds of 0.30 ± 0.09 m/s (left column) and 1.22 ± 0.38 m/s (middle column), as well as the apex of an unpolished sample (right). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. Energy dispersive x-ray map images were obtained by FEI Verios 460 SEM with an Oxford X-Max 80 mm² Energy Dispersive Spectrometer detector.

The Si & O EDX maps in Figure 7 appeared to confirm that the particles not intrinsic parts of the MCD coating were highly oxygenated in comparison to the rest of the surface. It was also noted from these images that some silicon may also be on some of these particles, though this appeared to be mostly insignificant, excluding the sample polished at highest normal force (5.2 ± 0.2 N) with highest sliding speed (1.22 ± 0.38 m/s), which appeared to show some significant concentration of silicon on these oxygenated particles. Due to the insignificant level of silicon observed and the oxygenated particles on unpolished samples, the evidence gathered from these EDX maps revealed there being little or no chemical difference between the MCD surface before and after polishing and cleaning. This evidence therefore supported the MCD coating

had not been removed from the SiC, and the chemical reactants and products (expected from CMP by the method employed) had been effectively removed by the cleaning process.

4.3. Optical profilometry results

The results obtained by optical profilometry before processing using MultiFile Analyzer are displayed in Appendices A4 and A5. These results were subsequently processed by removing the spherical background and adjusting the false colour height ranges so that ~95 % of the bell curve of heights associated with each image was fit within the height range colour bar to reduce influence from outliers (any outliers in either direction were matched to the most extreme false colour in the associated height direction), and the middle of each height colour range correlated to the median height. The processed optical profilometry images are displayed below in Figure 8 and Figure 9.

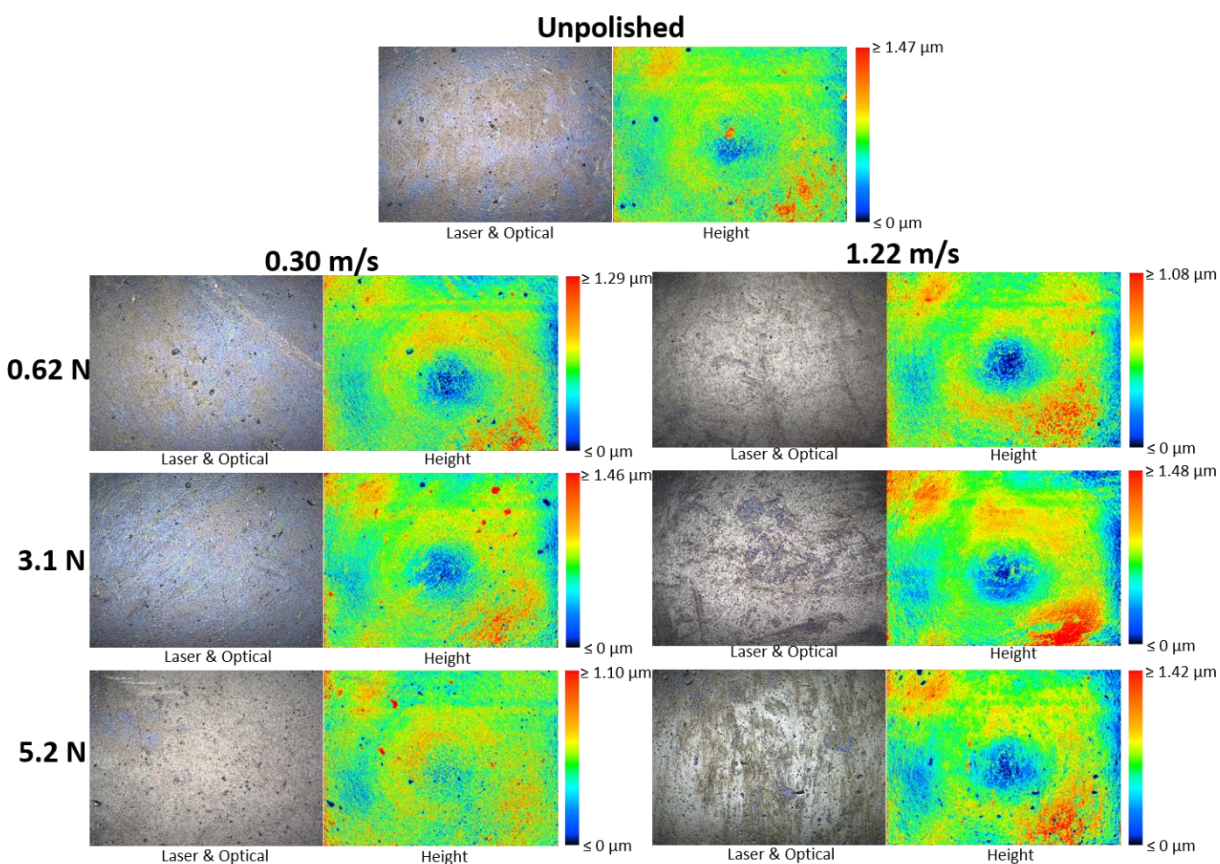


Figure 8: Optical focus variation profilometry paired images ($702 \mu\text{m} \times 526 \mu\text{m}$, 686 nm / pixel and 659 nm / pixel respectively) (laser & optical on left, height on right of each pair) of the apex area of B-doped (2000 – 4000 ppm) microcrystalline-diamond-coated SiC hemispheres (3 mm diameter) subject to chemical mechanical polishing using normal forces of $0.62 \pm 0.21 \text{ N}$ (2nd row), $3.1 \pm 0.2 \text{ N}$ (3rd row) and $5.2 \pm 0.2 \text{ N}$ (bottom row) and average sliding speeds of $0.30 \pm 0.09 \text{ m/s}$ (left column of bottom 3

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rows) and 1.22 ± 0.38 m/s (right column of bottom 3 rows), as well as the apex area of an unpolished sample (top). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. Images were obtained using laser-scanning confocal microscope (Keyence VK-X1000) and were processed by Keyence MultiFile Analyzer to remove the spherical background and fit ~95 % of the bell curve of heights into the false colour for height range with the median in the centre of the height range.

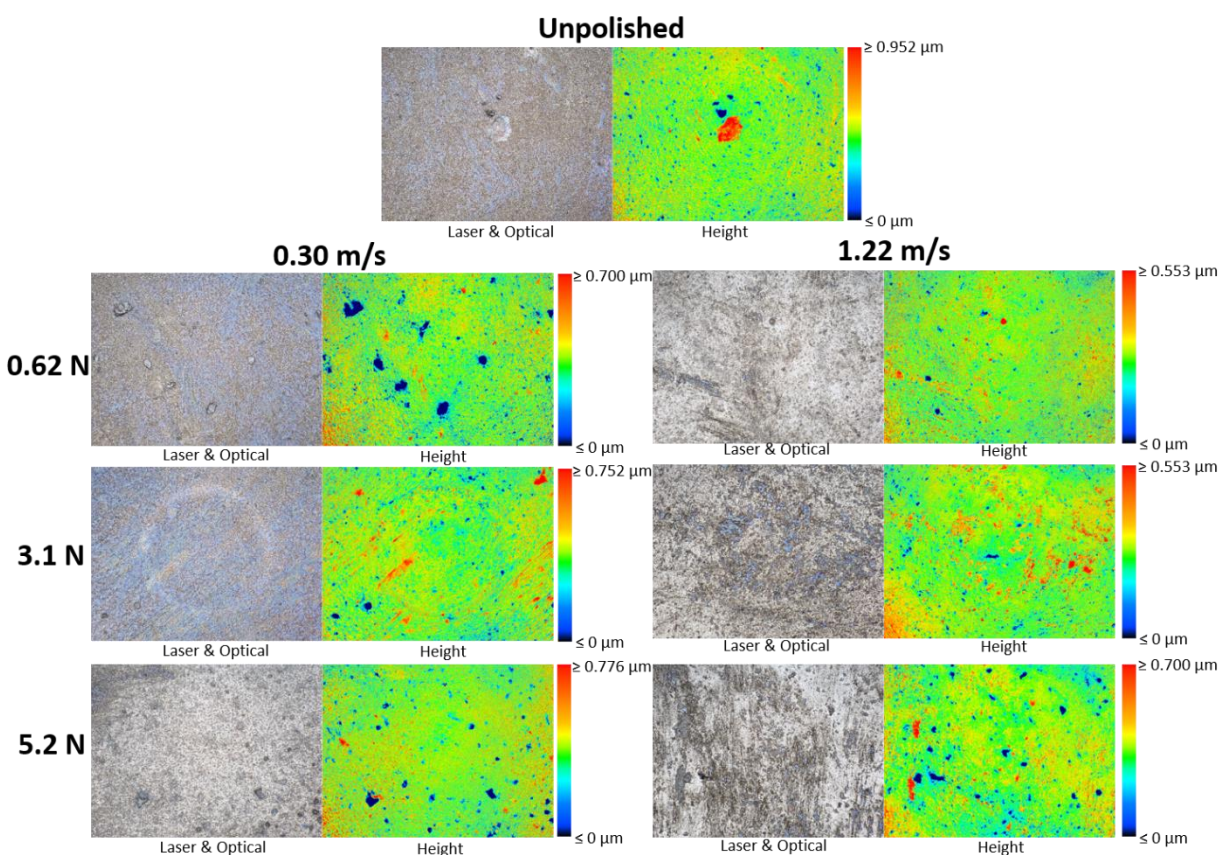


Figure 9: Optical focus variation profilometry paired images ($283 \mu\text{m} \times 212 \mu\text{m}$, $138 \text{ nm} / \text{pixel}$ along both axes) (laser & optical on left, height on right of each pair) of the apex area of B-doped (2000 – 4000 ppm) microcrystalline-diamond-coated SiC hemispheres (3 mm diameter) subject to chemical mechanical polishing using normal forces of 0.62 ± 0.21 N (2nd row), 3.1 ± 0.2 N (3rd row) and 5.2 ± 0.2 N (bottom row) and sliding speed averages of 0.30 ± 0.09 m/s (left column of bottom 3 rows) and 1.22 ± 0.38 m/s (right column of bottom 3 rows), as well as the apex area of an unpolished sample (top). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. Images were obtained using laser-scanning confocal microscope (Keyence VK-X1000) and were processed by Keyence MultiFile Analyzer to remove the spherical background and fit ~95 % of the bell curve of heights into the false colour for height range with the median in the centre of the height range.

The height ranges differed across all samples within both Figure 8 and Figure 9, though they considered of significant enough similarity to make some comparative assessments. From all the height images within these optical profilometry results it was observed that the holes identified before in the MCD surfaces, were also identified in all these results. It was noted that the heights within the images of the surfaces in Figure 8 appeared to be significantly lower in a

central area around the apex and significantly higher in a “ring” around that central area. It was considered that this height variation was more significant in samples polished at the highest speed (1.22 ± 0.38 m/s), potentially considered to be polished to greater effect at the apex, it was proposed that this variation may be due to the spherical background removal process using the software, this is illustrated to demonstrate extreme cases in Appendix A13. It was understood that due to the size of the areas being measured, especially with respect to the smaller ($283 \mu\text{m} \times 212 \mu\text{m}$) images, this variation in spherical background removal may introduce some data skewing, but not to large enough extent as to remove the validity of highly significant observations. The height images within Figure 8 appeared to show a significant reduction in height of the central apex area of each polished sample compared to that of the unpolished sample, excluding in the case of the sample polished at highest normal force (5.2 ± 0.2 N) with lowest sliding speed (0.30 ± 0.09 m/s), where the central apex area appeared to be similar to that of the unpolished sample. This was taken as supporting evidence that the CMP process had been effective in material removal from the MCD surface and there was a range of extents to which the material removal had taken place across the samples polished using different combinations of normal forces and sliding speeds. It was also noted that from the height images of Figure 8 that the samples polished at the highest sliding speed (1.22 ± 0.38 m/s) showed significantly lower height (deeper blue) and larger area of low height (blue) in comparison to the samples polished at the lowest sliding speed. It was noted from this observation that sliding speed appeared to show a significant and positive correlation with MCD surface material removal at this scale. From further observation of the images in Figure 8, excluding the case of the sample polished at the highest normal force and lowest sliding speed, normal force appeared to show no significant correlation with material removal across the samples polished at either sliding speed. This was taken as evidence that normal force had little or no effect on sliding speed at this scale. All of the observations from the images in Figure 8 where height lowering in the centre area was considered as material removal, also appeared in positive correlation with height rises (orange to red) in the ring area surrounding each central apex area.

It was noted from observing all the laser and optical images from Figure 8 and Figure 9, that the colour of the hemispheres appeared very similar across the samples polished at the lowest (0.62 ± 0.21 N) and medium (3.1 ± 0.2 N) normal forces with the lowest sliding speed (0.30 ± 0.09 m/s) and the unpolished sample, being mainly beige and blue, whilst the remaining polished samples appeared more colourless. It was also noted from these laser and optical images that marking and/or scratches were present on the samples polished, excluding the samples polished at both the lowest normal force and highest (5.2 ± 0.2 N) normal force with the lowest sliding speed, this marking and/or scratching appeared more significant in the samples polished at the highest sliding speed (1.22 ± 0.38 m/s). The significance of the marking and/or scratching within the samples polished at the highest sliding speed appeared in positive correlation with normal force. From these observations of colour change and notable marking/scratching, more supporting evidence was obtained that change in surface topography had a significant and positive correlation with both sliding speed and normal force, where sliding speed had greater positive correlation with change in surface topography in comparison to applied normal force during CMP at these scales.

It was revealed that the smallest identified area of significant polishing ($248 \mu\text{m} \times 168 \mu\text{m}$, image from sample polished at 3.1 ± 0.2 N and 1.22 ± 0.38 m/s) was smaller than the optical profilometry images of highest magnification ($283 \mu\text{m} \times 212 \mu\text{m}$). These highest magnification images were therefore used in the quantitative analysis, through production of representable circular areas with each circle centre as the apex of each sample for effective comparison of the results of the CMP performed. The resulting circles for effective comparison were each of diameter $195 \mu\text{m}$, whilst this was bigger than the smallest dimension of the smallest identified area of significant polishing of a sample ($168 \mu\text{m}$) according to the lower magnification images, the higher magnification images and SEM images (Figure 5) appeared to demonstrate that the polished areas were largely similar to this size across all samples. To further process the images, outlying heights from holes, abnormally large peaks, and particles not intrinsically part of the MCD coating structure were identified by-eye and removed (the software did not allow for quantitative removal of outliers according to height ranges). This image processing of each sample is illustrated in Appendix A14. The resulting circular images (Appendix A15) were

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analysed by MultiFile analyser software to produce RMS roughness, Sdq and Spc values, displayed in Figure 10.

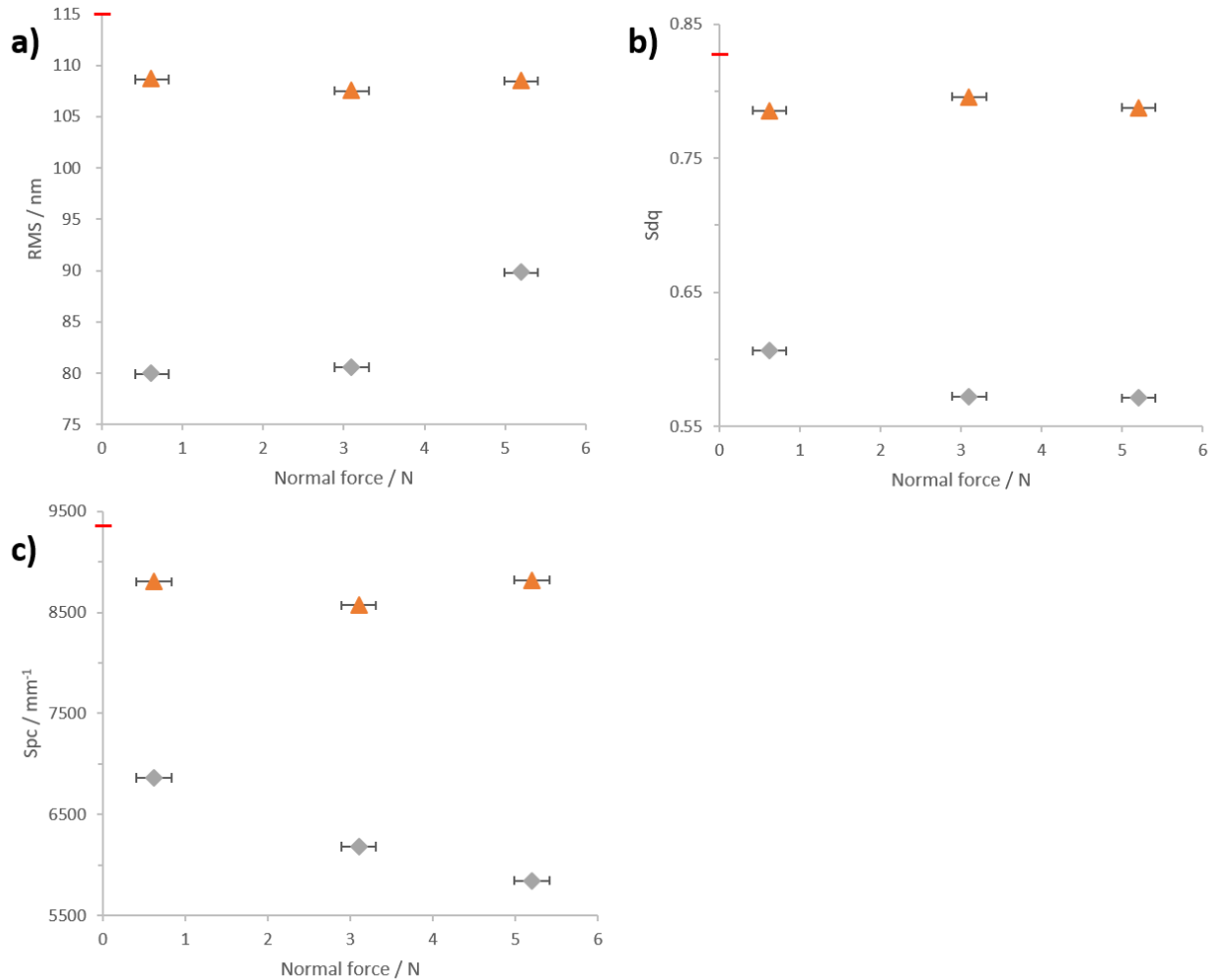


Figure 10: Resulting RMS roughness (a), Sdq (b) and Spc (c) within the apex area of B-doped (2000 - 4000 ppm) microcrystalline diamond coated (MCD) SiC hemisphere samples (3 mm diameter) subject to chemical mechanical polishing using different normal forces and 0.30 ± 0.09 m/s (orange triangles) and 1.22 ± 0.38 m/s (grey diamonds) average sliding speeds, as well as comparisons against unpolished samples (red lines). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. Results were measured by Keyence 3D laser confocal profilometer and assessed over a $195 \mu\text{m}$ diameter circle of the apex with background spherical surface removal and removal of outlying asperities using Keyence MultiFile Analyzer.

From the result values observed in Figure 10, it was noted that there was a significant and positive correlation between applied sliding speed during CMP and change in topography over the polished apex area. It was also observed from these results that any correlation between normal force and change in topography was much less significant than the positive correlation identified between change in topography and applied sliding speed, especially where the

lowest sliding speed (0.30 ± 0.09 m/s) was applied, as seen by the range of resulting RMS roughness, Sdq and Spc values related to each parameter. The samples polished at the lowest sliding speed were taken as not providing significant enough variation in the RMS, Sdq and Spc results to take any correlations as evidence. From the results observed from samples subject to the highest sliding speed (1.22 ± 0.38 m/s), the RMS roughness values appeared to reveal a slight positive correlation with applied normal force across the samples polishing at the lowest (0.62 ± 0.21 N) and the medium (3.1 ± 0.2 N) normal forces, with a much higher positive correlation observed between the samples polished at the medium and highest normal force (5.2 ± 0.2 N). Furthermore, the samples polished at the highest sliding speed appeared to show significant negative correlation between normal force and Spc. Within the samples polished at the highest sliding speed, the combination of positive correlation between normal force and RMS, and negative correlations between normal force and both Spc and Sdq was taken to align well with the proposed idea that the variation in spherical background removal had affected the quantitative results (Appendix A13). All the observations obtained from Figure 10 provide evidence that polishing had been effective, as all RMS roughness, Sdq and Spc values were significantly lower in the samples subject to CMP, compared to the unpolished sample. In addition, evidence was obtained that applied sliding speed had a much more significant impact on the topography of the diamond coating compared to applied normal force, and both normal force and sliding speed appeared to be in positive correlation with change in surface topography, with the exception of the samples polished at the lowest sliding speed which did not produce effectively significant results.

4.4. AFM results

Due to error during analysis and lack of time, the number of AFM micrographs ($5 \mu\text{m} \times 5 \mu\text{m}$) obtained per sample were significantly unequal (ranging from 3 to 8 images per sample), though at least three suitable images were obtained from each polished sample, and one suitable image of each unpolished sample, which was expected to result in AFM results with statistical validity of some significance. All the suitable AFM micrographs (without significant error observed e.g. from loss of uniform cantilever angle variation due to extreme sudden changes in height (usually from holes in the MCD coating)) were used to take advantage of all

available data and because the mean averages of the data results from each sample were used to reduce bias. The AFM micrographs obtained were processed using Gwyddion by levelling the data by mean plane subtraction, aligning all rows by polynomial degree of 2 and correcting horizontal scars, this produced representable images of the surfaces with minimal interference from background noise and without the spherical background of the sample. Using the same software, RMS roughness and Sdq values were obtained for each processed AFM micrograph, for display purposes for the reader/s a representable image for each sample was obtained by matching the sample micrograph with closest RMS roughness and Sdq values to the mean average result of that sample, these resulting representable AFM micrographs are displayed in Appendix A16. It was noted from all obtained AFM micrographs through observation specifically in the zx and zy plane directions that significant holes from improper MCD growth were present, the images were therefore cropped to remove the outlying holes, as there was no pure quantitative way to remove these outliers using the software available. After cropping, the RMS roughness and Sdq values were again obtained, these are displayed in Appendix A17. Once again for the reader/s, representable images were obtained for these cropped images using the same method as outlined above, these images are displayed in Appendix A18. Figure 11 displays the mean results with standard deviation errors of the cropped image RMS roughness and Sdq values to represent the results of each sample.

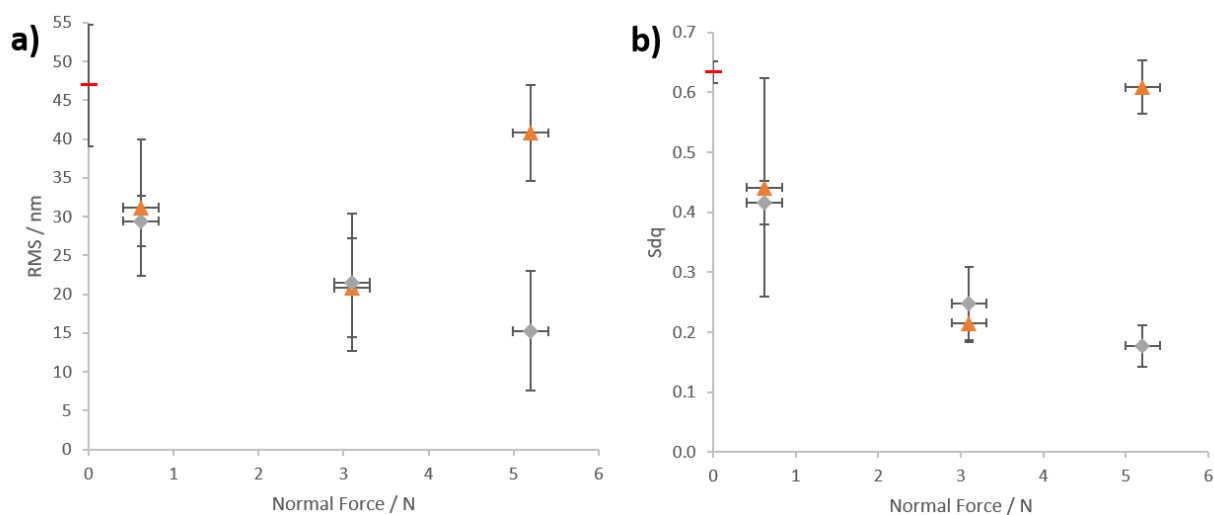


Figure 11: Resulting RMS roughness (a) and Sdq (b) within the apex area ($\sim 100 \mu\text{m} \times 100 \mu\text{m}$) of B-doped (2000 - 4000 ppm) microcrystalline diamond coated (MCD) SiC hemisphere samples (3 mm diameter) subject to chemical mechanical polishing using different normal forces and average sliding speeds of $0.30 \pm 0.09 \text{ m/s}$ (orange triangles) and $1.22 \pm 0.38 \text{ m/s}$ (grey

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diamonds), as well as comparisons against unpolished samples (red lines). Chemical mechanical polishing was performed for 10 minutes using colloidal silica (70 nm diameter) in deionized water (17 % weight/volume, pH 9, 0.18 L/min) with a SUBA X (polyurethane impregnated polyester pad) and a Struers LaboPol-5 polishing machine. Results were measured over $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ areas within the apex area by a Bruker ICON atomic force microscope, using a RTESPA 300-30 (30 nm diameter) probe in tapping mode in air, in standard ambient temperature and pressure conditions. Results were processed and assessed by use of Gwyddion by levelling data by mean plane subtraction, aligning rows by polynomial degree of 2 (to remove spherical surface background) and correcting horizontal scars, followed by cropping of the images to remove outlying holes due to errors in the MCD coating growth.

The first observation of Figure 11, was that except for samples polished at the lowest sliding speed ($0.30 \pm 0.09\text{ m/s}$) with the highest normal force ($5.2 \pm 0.2\text{ N}$), all the polished samples exhibited lower RMS roughness and Sdq mean averages in comparison to the unpolished sample. It was also noted from Figure 11 that there was highly significant overlap within the RMS and Sdq results produced from both sliding speeds where the lowest ($0.62 \pm 0.21\text{ N}$) and medium ($3.1 \pm 0.2\text{ N}$) normal forces were applied, therefore demonstrating that sliding speed had an insignificant effect on change in surface topography at this scale, excluding the sample polished at the highest normal force and the lowest sliding speed. There was significant evidence of a strong and significant negative correlation between normal force and both RMS roughness and Sdq values with both sliding speeds, excluding the sample polished at the lowest sliding speed with the highest normal force which revealed RMS and Sdq values largely similar to the unpolished samples.

4.5. Discussion

Due to significant changes in RMS, Spc Sdq values produced by the CMP method applied observed by use of quantitative AFM and optical profilometry results, as well as qualitative differences observed by SEM between polished and unpolished samples, aligned with SEM images and EDX maps revealing insignificant concentrations of silicon and oxygen on the surface, the CMP process with subsequent cleaning is believed to be effective in producing variations in topography of the MCD coating without exposing the SiC substrate or leaving polishing consumables or products remaining on the MCD surface. Development of an effective laboratory setup for CMP of MCD films was therefore successful.

When combining the evidence gathered from the results, it was noted that normal force exerted on the MCD coated hemispheres was expected to be distributed across the surface area exposed to both polishing slurry and polishing pad, and due to the hemispherical shape of

the MCD surface, the area pushed deepest into the pad and slurry (assumed as the apex) was expected to be acted upon by the greatest normal force. Greater distance from the apex with greatest normal force acting upon it into the pad and slurry, would result in lower acting normal force upon that section of MCD surface, and would also have a direct effect on the pressure acting upon the slurry in that section, with a positive correlation between effective normal force and effective pressure upon the slurry. As mentioned in the introduction, increased sliding speed produces a greater bearing capacity of the fluid film due to increased flow rate introduced via the polishing pad. The quantitative results of optical profilometry demonstrated a significant positive correlation between sliding speed and change in RMS, Spc and Sdq values, though a mainly insignificant correlation between normal force and change in RMS, Spc and Sdq. On first observation, this was displaying a highly controversial trend to that observed by the quantitative results from AFM, which displayed a significant positive correlation between normal force change in RMS, Spc and Sdq values, and an insignificant correlation between sliding speed and change in RMS, Spc and Sdq, excluding the results obtained at highest normal force and lowest sliding speed. However, when the scales were taken into consideration, along with the understanding that the samples are hemispherical and although the polishing pad is softer than diamond it still was of significant hardness, some effective hypotheses were obtained. It was noted that during polishing of each sample, as would be expected, slurry was “pushed” up the sides of the area in greater contact with the polishing pad, at these sides the polishing pad interaction was considered as absent. Although the polishing pad is highly significant in the CMP method applied, this area of ineffective interaction with the polishing pad would still be polished to some extent by the abrasive action of the slurry (although with significantly less normal force/pressure acting upon it) and/or viscous friction. Although applied pressure upon this area from the spring and interaction with the pad was effectively insignificant, sliding speed – and therefore flow rate of the slurry – would be expected to reveal a positive correlation with material removal and change in RMS, Spc and Sdq values. This would explain the results observed from the optical profilometry results as they could include areas not subject to effective interaction with the polishing pad, due to the larger sample size of 195 μm diameter, compared to the sample area of the AFM analyses being approximately half of

that ($100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$) and therefore influenced to a much higher significance by effective interaction with the polishing pad. Results by atomic force microscopy were taken to be significantly more sensitive to changes in surface topography as well as obtained within an area closer to the apex of each sample, which supported the AFM being more representative of the results where pad and slurry were both significantly involved in the CMP process. The results from AFM displayed a highly significant positive correlation between normal force and changes in RMS, Sdq and Spc, though where the highest normal force was employed, there was a large difference between the sample polished at the lowest sliding speed and the sample polished at the highest sliding speed. This large difference was taken to be due to the requirement of slurry to enter the interfacial region between the polishing pad and MCD coating, for effective CMP of diamond to take place. At lower sliding speed, the flow rate into the interfacial region is lower and the bearing capacity of the fluid film is reduced. Therefore, where the applied normal force is highest and the sliding speed is the lowest, the effective pressure acting upon the slurry fluid film was taken to be overcome and the slurry inhibited from entering the interfacial region, disabling the proposed CMP mechanism from taking place and instead interaction between polishing pad and MCD coating would be dominated by friction, with minimal change in MCD coating topography due to the much greater hardness of diamond compared to the polishing pad. This explanation was taken to reveal that the area of polishing was less than $195\text{ }\mu\text{m}$ in diameter and that normal force was of much higher significance to changing the surface topography by this CMP method, however this would only be the case if the sliding speed is high enough to maintain a fluid film bearing capacity large enough to withstand the applied normal forces. This hypothesis appears to align well with recent literature (2.5. Relevant Influences on CMP of Diamond), being that increasing normal force increases decomposition and bonding of the resulting products of water to diamond surfaces, as well as increasing mechanochemical interaction and carbon removal by interaction between silica abrasive and oxygenated diamond surface during this method of CMP, as well as flow rate of slurry into the interfacial region needing to be high enough for this CMP method to be effective. ^{7, 42, 43, 48-52}

It was noted that observations of the larger SEM images (Figure 5) showed some correlation with the results obtained from AFM, with greater amount of the particles not intrinsic to the

MCD coating produced under higher normal forces at higher sliding speed and the same at lower sliding speeds excluding the case of where the higher normal force was applied. Some similarity between the optical profilometry results and the smaller SEM images (Figure 6) was also noted, where higher sliding speed produced greater change in topography. However, the SEM images contained no purely quantitative data and directing analysis to the central apex area under SEM was only by an estimated approach, so the SEM results whilst considered as useful, were not considered as overriding evidence against the quantitative optical profilometry and AFM results.

It was noted that there were many limitations when producing the results for this report, mainly time, which influenced many factors, including the ability to investigate a larger number of samples (repeats and more effective spread of applied normal forces and sliding speeds), and therefore the hypotheses from this discussion is proposed to only be considered preliminary until further investigation can be undertaken.

4.6. Future Directions

To produce a fuller picture of the influence of different polishing parameters on the MCD topography and tribological behaviour, many methods or improvements on the methods used in this report are suggested below:

- Due to limitations of both software applications used to process data - MultiFile Analyzer and Gwyddion – quantitative removal of outliers was not possible, therefore using a software with these capabilities is advised.
- Tribological simulation models such as the Boundary Element Method (BEM), could be applied to determine both the normal force distribution, and the effective contact area distribution of the polishing pad, on the MCD surface topography.
- Greater variety of normal forces could be applied; mainly greater number of applied normal forces between 0.62 ± 0.21 N and 5.2 ± 0.2 N, as well as normal forces higher than 5.2 ± 0.2 N and lower than 0.62 ± 0.21 N. This would be useful in confirming the proposed hypothesis involving effective contact with the polishing pad and fluid film

bearing capacity against the polishing parameters applied and the resulting material removal mechanisms.

- Identifying the area of CMP directly affected by interaction with the polishing pad within the optical profilometry images, would be useful to compare these areas across the samples, and identify differences in polishing where pad, diamond coating and slurry are all effectively involved. Also, removal of this area identified as involving effective interaction with the pad, would enable comparison of change in surface topography due to CMP at different normal force and sliding speeds, where just the slurry and diamond coating is considered as effectively interacting.
- The number of samples subject to CMP were few and the number of AFM micrographs obtained per sample were unequal, which both reduce statistical validity. To produce effective data, a greater number of samples for each normal force and sliding speed pairing and an equal number of analysis results per sample should be obtained.
- To investigate the influence of the polishing parameters in more depth, maintaining normal force and sliding speed but obtaining quantitative results according to CMP duration could further unveil the tribological behaviour and change in topography.
- A fixed position for the samples on the polishing pad would significantly reduce error of the relative sliding speed during CMP.
- Profilometry images could be obtained of each sample before and after polishing, where the orientation of the samples is maintained, the resulting images could then be overlapped for each sample to produce direct comparative changes of topography due to the CMP performed.
- To investigate variations in topography according to the distance from the sample apex when varying polishing parameters are applied, the circular images obtained through profilometry could be gathered in smaller and larger sizes or ring images obtained and many comparisons made accordingly, including the effect of sliding speed and normal force at different distances from each sample apex.
- The presence of holes and other unwanted topographical effects due to ineffective seeding and MCD growth resulted in the samples appearing to show inconsistency

before CMP was performed, obtaining samples without these issues would reduce analysis time and improve data quality.

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