Polishing of {100} and {111} single crystal diamond through the use of Chemical Mechanical Polishing

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Abstract

Diamond is one of the hardest and most difficult to polish materials. In this paper, the polishing of {111} and {100} single crystal diamond surfaces by standard Chemical Mechanical Polishing, as used in the silicon industry, is demonstrated. A Logitech Tribo Chemical Mechanical Polishing system with Logitech SF1 Syton and a polyurethane/polyester polishing pad was used. A reduction in roughness from 0.92 to 0.23 nm root mean square (RMS) and 0.31 to 0.09 nm RMS for {100} and {111} samples respectively was observed.

1 Introduction

Diamond has long been used for cutting and polishing applications due to its extreme hardness, high thermal conductivity and chemical inertness. However, properties such as a large band gap,
high resistivity, high electron mobility, low dielectric constant, and low thermal coefficient of expansion make diamond an excellent candidate for high power - high frequency electronics,\textsuperscript{1,2} and optical devices.\textsuperscript{3,4} With the advancement of technology it is now possible to economically synthesize high quality large area single crystal diamonds through homoepitaxial CVD.\textsuperscript{5,6} However, to prevent defects and surface damage from the substrate from propagating into the CVD layer a polishing step is required.\textsuperscript{7} Recent experiments have also pointed to the presence of two dimensional hole gas on the surface of hydrogen terminated diamond.\textsuperscript{8} To harness this phenomenon, and for the applications mentioned above, it is also important to have atomically flat, defect free top surfaces - necessitating an efficient polishing technique.

For the polishing of diamond, while many techniques exist including thermo-mechanical, ion beam, and thermal annealing, mechanical polishing has traditionally prevailed.\textsuperscript{9–14} Mechanical polishing is typically done through the use of a fast rotating metal scaife charged with a diamond grit and olive oil binder. The sample is polished by putting it under pressures of 2.5-6.5 MPa for grinding and 1-2.5 MPa for polishing against a scaife with linear velocity of approximately 50 m/s.\textsuperscript{15} However, the polishing of diamond is highly anisotropic with two orders of magnitude difference in removal rate between hard and soft polishing directions for the \{100\} and \{110\} plane groups.\textsuperscript{16} Along soft directions polishing is the result of shearing between diamond chips on the scaife and the sample surface, driving a phase conversion to non sp\textsuperscript{3} material.\textsuperscript{17} As a result ‘nano-grooves’ are found on the surface with lengths of 20 - 1000 nm dependent on the grit used and depths of up to 20 nm, whereas, polishing along hard directions leads to fracturing along the \{111\} plane producing a rough ‘hill and valley’ type surface.\textsuperscript{18} Polishing of the \{111\} plane meanwhile remains difficult,\textsuperscript{19} with only slight anisotropy between hard and softer polishing direction.\textsuperscript{3} Due to the inherent mechanical nature of this technique subsurface damage occurs, with fractures at the surface propagating into the bulk.\textsuperscript{20} This problem of poor surface quality is often seen in the techniques mentioned above, preventing full use of the properties of diamond.\textsuperscript{21}

In order to reduce these polishing artifacts several methods have been proposed as a finishing technique, including chemo-mechanical\textsuperscript{22–24} or tribochemical polishing,\textsuperscript{25} and reactive ion
In chemo-mechanical polishing a molten oxidizer is added, typically KNO₃ (potassium nitrate), NaNO₃ (sodium nitrate), or H₂O₂ (hydrogen peroxide). Between the scaife and diamond sample hot spots of 360 °C are reached driving a conversion to CO and CO₂. While this method achieves low roughness values, the use of scaife and elevated temperatures makes the process complicated and very different to that used in the silicon based electronics industry.

Previous work by the authors have shown Chemical Mechanical Polishing, a technique used in the polishing of gate dielectrics in IC fabrication, can successfully be used to polish Nanocrystalline Diamond (NCD) films. In this technique the sample is swept across the polyester/polyurethane based polishing pad doused with colloidal silica polishing fluid (Syton) without the use of any diamond grit or elevated temperatures. Drawing parallels with the mechanism used to describe the polishing of SiO₂, it was tentatively suggested that wet oxidation of the diamond increases the hydroxide content on the surface, facilitating the binding of silica particles within the slurry. Should an asperity on the rough pad then create a sufficient shearing force on the silica particle, the particle and attached carbon atom will be removed, polishing the surface.

In this article the use of CMP on {100} and {111} single crystal diamond is demonstrated through the use of Atomic Force Microscopy (AFM). The aspects of this adaption from the IC fabrication industry, including the condition of the polishing pad and post polishing cleaning is also been discussed.

2 Experimental Method

HPHT Single Crystal {100} and {111} samples were obtained from Elementsix. The {100} sample was approximately 2 by 2 by 0.5 mm high, whereas the {111} sample was 3 by 3 by 0.7 mm high. Before use both samples were given a standard SC-1 clean of 30% H₂O₂: NH₄OH:DI H₂O (1:1:5) at 75 °C for 10 min, followed by a ultrasonic DI H₂O bath for 10 minutes. In preparation for polishing, samples were bonded within a slight recess on a 2-inch polymer holder with cyanoacrylate. The recess was then filled up with Crystalbond to prevent shear forces on crystal
edges, ensuring a stable mounting while leaving only the surface to be polished protruding. This template was then placed inside a carrier chuck suitable for use with the CMP equipment.

Chemical Mechanical Polishing was carried out with a Logitech Tribo CMP tool equipped with a SUBA - X polyester/polyurethane pad and Syton colloidal silica alkaline polishing fluid (15-50% SiO$_2$, 9.2-10.1 pH, 4-5% ethylene glycol), as described elsewhere. Before, and during use, the polishing pad was conditioned to maintain a rough surface to maximize polishing action and to efficiently distribute polishing slurry. During polishing both holder and pad were kept rotating at 60 rpm in opposite directions as the holder swept across the pad. Down pressure on the holder was maintained at 4 psi while a backing pressure of 20 psi was applied to prevent bowing of the holder and ensure contact between the diamond crystal and the polishing pad. After initial wetting of the plate, the polishing slurry rate was maintained at 40 ml/min. Polishing durations for the {100} and {111} single crystals were 3 and 7 hours respectively. After polishing, the samples were cleaned with SC-1 and Hydrofluoric Acid in an attempt to remove any organic contaminants and remaining silica.

Atomic Force Microscopy was performed with a Park Systems XE-100 AFM operating in non-contact mode equipped with NT-MDT NSG30 tips (320 kHz resonant frequency, 40 N/m spring constant, 10 nm tip radius). Multiple areas of 5 × 5 µm$^2$ were scanned for each sample before and after polishing, with analysis of data being carried out by WSxM and Gwyddion SPM analysis software.

For analysis of the polishing pad, samples were taken of: a fresh pad, a conditioned pad, and a pad that had been subjected to 7 hours of single crystal polishing. Scanning Electron Microscopy (SEM) images were taken with the SE2 detector of a Raith E-line SEM, operating at 10 kV accelerator voltage and 9 mm working distance.
Figure 1: AFM images of a {100} orientated single crystal before (A) and after chemical mechanical polishing (B). Shown in panels C and D are line traces perpendicular to the mechanical polishing direction (1) and along the polishing direction (2) of the respective AFM images. Clear removal of the mechanically induced phase transformation nano-grooves can be seen in the AFM images, backed up by the dramatic reduction in amplitude of the perpendicular to polishing direction line trace.

3 Results and Discussions

3.1 {100} Single Crystal

Typical AFM scans of the {100} single crystal before and after polishing are shown in panels A and B of Fig. 1 while lines traces perpendicular to polishing direction (1), and along the polishing direction (2) are plotted in panels C and D. As can be seen in panels A and C, the surface of the sample prior to CMP consists of clearly defined “nano-grooves” as a result of the nanodiamond particle induced phase transformation along the $<100>$ soft direction. From the 5 $\mu$m perpendicular line trace it can be seen that the nano-grooves widths are between 100 and 500 nm and that they have an average depth of 3 nm. Meanwhile, for the trace along the polishing direction less variation is seen with little indication of fracture. Roughness values are 0.92 nm RMS and 0.34
Figure 2: AFM images of the \{111\} polished plane before (A) and after chemical mechanical polishing (B). Shown in panels C and D are line traces similar in fashion to those seen in Fig. 1B. Once again, a clear removal of grooved surface features can be seen, leading to a very smooth surface with line trace roughness reducing from 0.31 and 0.23 nm RMS for perpendicular to and along original polishing direction to 0.09 nm RMS.

Looking at the 3 hour CMP polished AFM image and line traces of Fig. 1B and Fig. 1D a clear difference can be seen with the removal of the mechanical polishing scuff marks to the point at which it is difficult to resolve the original polishing direction. The line trace perpendicular to the polishing direction shows a decrease in the larger undulations of the nano-grooves to a point at which it is in close agreement with the trace taken along the original polishing direction, with roughness values being 0.23 and 0.19 nm RMS respectively. It is also worth noting that a lack of polishing debris can be seen in the polished AFM image, showing the ease of removal of the polishing slurry used.
3.2 \{111\} Single Crystal

As with the \{100\} single crystal sample, Fig. 2 shows typical AFM images of the \{111\} single crystal before and after being subjected to 7 hours of CMP along with line traces perpendicular (1), and along the mechanical polishing direction (2). As can be seen from panel A, the \{111\} single crystal has similar, but shallower, grooved features as the \{100\} crystal. Roughness values seen perpendicular to and along the original polishing direction are 0.31 nm and 0.23 nm RMS respectively. After being subjected to CMP it is again very difficult to determine the original polishing direction due to the dramatic reduction in the grooved features. Looking at the two perpendicular line traces they appear very similar, reiterating the removal of these grooves. Roughness values for these traces are significantly lower at 0.09 nm RMS for both perpendicular and along the polishing direction traces.
3.3 Polishing Pad

The condition and properties of the polishing pad heavily dictate the wear rate and uniformity of the resulting diamond surface.\textsuperscript{29–32} In traditional CMP it has been seen that the removal rate is directly related to the surface roughness and hence number of asperities of the polishing pad.\textsuperscript{32} However, the pad also needs to be porous to allow for slurry distribution and clearing away of spent material. To increase this surface roughness and increase the porosity, pads are typically ‘run in’\textsuperscript{31} or ‘conditioned’ before use with an electroplated diamond grit plate. Upon polishing the pad is then plastically deformed by the sample, closing pores and reducing the number of these surface asperities in as little as 10 minutes.\textsuperscript{31} While the diamond samples themselves will condition the pad surface, due to the polishing duration being in the hours rather than minutes,\textsuperscript{31} in-situ conditioning of the pad is also needed. Due to the difference in mechanical properties of diamond and the materials traditionally polished with these polyester/polyurethane pads, work is needed to characterize the pad during diamond polishing.

SEM images of an as received SUBA-X polishing pad, a conditioned pad, and a pad subjected to 7 hours of single crystal CMP can be seen in Fig. 3A to 3C. From the fresh pad the polyester strands can be seen to be bound together by the dense polyurethane foam. After being conditioned, the abrasion by the electroplated diamond grit can be seen. Polyester strands are less uniformly orientated, if not cut, and the polyurethane binder has opened up and become rougher at the magnification used. It can therefore be assumed that conditioning has increased the surface asperities on a scale closer to the size of the silica particles. Wear tracks visible by eye were observed on the pad after 7 hours suggesting significant abrasion is carried out by the diamond surfaces. The corresponding SEM image also shows this wear with most of the polyester strands being severed and polyurethane foam appearing severely abraded.

3.4 Discussion

Looking at the AFM images for the \{100\} and \{111\} orientated single crystals of Fig. 1 and 2, a clear polishing effect can be seen. The deep nano-grooves left over from mechanical polishing
have been removed, leaving a smoother surface over the 25 \( \mu m^2 \) image area. The line trace perpendicular to these polishing grooves reiterate this with a reduction in roughness from 0.92 to 0.23 nm RMS and 0.31 to 0.09 nm RMS for the \{100\} and \{111\} samples respectively. After polishing the line traces appear very similar to the traces along original polishing direction, again showing this clear removal. With regards to polishing rate, these roughness values show faster polishing on the \{100\} than the \{111\} plane as seen in mechanical polishing.

It is worth noting that no attempt was made at polishing along soft mechanical directions, with the sample being rotated while sweeping across the pad. Equal time was then spent polishing along hard and soft polishing directions with no indication of the fracture damage seen when mechanically polishing along hard directions, showing the gentle nature of the polishing mechanism used here. The surfaces are also free of polishing debris or remaining polishing slurry due to the combined use of SC-1 and HF cleaning after polishing, while it can also be assumed that there has been little to no increase in subsurface damage due to the lack of diamond grit being used in the polishing slurry. Due the difference in properties of diamond and the materials typically polished with CMP, study of the polishing pad is needed to optimize the adapted technique. Due to the hardness of diamond additional abrasion of the pad is seen, as highlighted in Fig. 3C, reducing the life time of the pad. When a harder EP1 pad was used scratching of the diamond crystal was seen demonstrating the importance of the pad.

It has been shown that CMP can be used efficiently to remove the scaife marks brought about through mechanical polishing of single crystal diamond and provide low roughness \{100\} and \{111\} diamond surfaces. With this technique polyester/polyurethane pads are used at room temperature with low applied pressures, without the use of diamond grit, simplifying the process and making CMP a promising technique.
4 Conclusion

\{100\} and \{111\} orientated single crystal diamond has been polished with Chemical Mechanical Polishing through the use of a polyester/polyurethane pad and an alkaline colloidal silica polishing fluid. Clear removal of the mechanical polishing induced nano-grooves can be seen, with \{100\} surface roughness values being reduced from 0.92 to 0.23 nm RMS along a 5 \(\mu\)m line trace taken perpendicular to the direction of the nano-grooves. Meanwhile, the equivalent line trace on the \{111\} sample shows a reduction from 0.31 to 0.09 nm RMS. Therefore with its simplicity due to the use of materials commonly found in the IC fabrication industry, along with the lack of diamond grit and elevated temperatures, CMP is a promising technique for removing mechanical polishing introduced artefacts.

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References

(1) Field, J. E. The properties of natural and synthetic diamond; Academic Press: London, 1992.

(2) Kohn, E.; Adamschik, M.; Schmid, P.; Denisenko, A.; Aleksov, A.; Ebert, W. Journal of Physics D: Applied Physics 2001, 34, R77.

(3) Schuelke, T.; Grotjohn, T. A. Diamond and Related Materials 2013, 32, 17–26.

(4) Teraji, T.; Yoshizaki, S.; Wada, H.; Hamada, M.; Ito, T. Diamond and Related Materials 2004, 13, 858–862.
(5) Isberg, J.; Hammersberg, J.; Johansson, E.; Wikström, T.; Twitchen, D. J.; Whitehead, A. J.; Coe, S. E.; Scarsbrook, G. A. *Science* **2002**, *297*, 1670–1672.

(6) Tallaire, A.; Achard, J.; Silva, F.; Sussmann, R. S.; Gicquel, A. *Diamond and Related Materials* **2005**, *14*, 249–254.

(7) Friel, I.; Clewes, S. L.; Dhillon, H. K.; Perkins, N.; Twitchen, D. J.; Scarsbrook, G. A. *Diamond and Related Materials* **2009**, *18*, 808–815.

(8) Hauf, M.; Simon, P.; Scifert, M.; Holleitner, W.; Stutzmann, M.; Garrido, J. *arXiv:1310.8616v1* 2013.

(9) Malshe, A. P.; Park, B. S.; Brown, W. D.; Naseem, H. A. *Diamond and Related Materials* **1999**, *8*, 1198–1213.

(10) Jin, S.; Graebner, J. E.; Kammlott, G. W.; Tiefel, T. H.; Kosinski, S. G.; Chen, L. H.; Fastnacht, R. A. *Applied Physics Letters* **1992**, *60*, 1948–1950.

(11) Suzuki, K.; Yasunaga, N.; Seki, Y.; Ide, A.; Watanabe, N.; Uematsu, T. *Proceedings of ASPE* **1996**, *482–485*.

(12) Hirata, A.; Tokura, H.; Yoshikawa, M. *Thin Solid Films* **1992**, *212*, 43–48.

(13) Ozkan, A. M.; Malshe, A. P.; Brown, W. D. *Diamond and Related Materials* **1997**, *6*, 1789–1798.

(14) Olsen, R. H.; Aspinwall, D. K.; Dewes, R. C. *Journal of Materials Processing Technology* **2004**, *155ü156*, 1227–1234.

(15) Chen, Y.; Zhang, L. *Polishing of Diamond Materials*; Springer: London, 2013; pp 25–44.

(16) Grillo, S. E.; Field, J. E. *Journal of Physics D: Applied Physics* **1997**, *30*, 202.

(17) Pastewka, L.; Moser, S.; Gumbsch, P.; Moseler, M. *Nature Materials* **2011**, *10*, 34–38.
(18) Hird, J. R.; Field, J. E. *Proceedings of the Royal Society of London Series a-Mathematical Physical and Engineering Sciences* **2004**, *460*, 3547–3568.

(19) Huisman, W. J.; Peters, J. F.; de Vries, S. A.; Vlieg, E.; Yang, W. S.; Derry, T. E.; van der Veen, J. F. *Surface Science* **1997**, *387*, 342–353.

(20) Volpe, P.-N.; Muret, P.; Omnes, F.; Achard, J.; Silva, F.; Brinza, O.; Gicquel, A. *Diamond and Related Materials* **2009**, *18*, 1205–1210.

(21) Gaisinskaya, A.; Edrei, R.; Hoffman, A.; Feldheim, Y. *Diamond and Related Materials* **2009**, *18*, 1466–1473.

(22) Kühnle, J.; Weis, O. *Surface Science* **1995**, *340*, 16–22.

(23) Kubota, A.; Fukuyama, S.; Ichimori, Y.; Touge, M. *Diamond and Related Materials* **2012**, *24*, 59–62.

(24) Wang, C. Y.; Zhang, F. L.; Kuang, T. C.; Chen, C. L. *Thin Solid Films* **2006**, *496*, 698–702.

(25) Haisma, J.; Vanderkruis, F.; Spierings, B.; Oomen, J. M.; Fey, F. *Precision Engineering-Journal of the American Society for Precision Engineering* **1992**, *14*, 20–27.

(26) Krishnan, M.; Nalaskowski, J. W.; Cook, L. M. *Chemical Reviews* **2009**, *110*, 178–204.

(27) Thomas, E. L. H.; Nelson, G. W.; Mandal, S.; Foord, J. S.; Williams, O. A. *Carbon* **2014**, *68*, 473–479.

(28) Hocheng, H.; Tsai, H. Y.; Su, Y. T. *Journal of the Electrochemical Society* **2001**, *148*, G581–G586.

(29) Hooper, B. J.; Byrne, G.; Galligan, S. *Journal of Materials Processing Technology* **2002**, *123*, 107–113.

(30) Lu, H.; Fookes, B.; Obeng, Y.; Machinski, S.; Richardson, K. A. *Materials Characterization* **2002**, *49*, 35–44.
(31) McGrath, J.; Davis, C. *Journal of Materials Processing Technology* **2004**, *153*, 666–673.

(32) Park, K. H.; Kim, H. J.; Chang, O. M.; Jeong, H. D. *Journal of Materials Processing Technology* **2007**, *187*, 73–76.