Highly-efficient and Ultra-smooth Polishing of Diamond via Atmospheric Pressure Inductively Coupled Plasma

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Abstract: In this study, we propose a novel method using atmospheric pressure inductively coupled plasma (ICP) to achieve damage-free and highly-efficient polishing of single crystal diamond (SCD) with a material removal rate (MRR) of 33.24 μm/min. The surface roughness of SCD can be decreased from 57.4 nm to 0.667 nm in only 15 min without impurity elements and structure defects being introduced. The technology we proposed presents expansive prospect in polishing diamond and promotes its further applications.

Keywords: SCD, ICP, ultra-smooth surface, highly efficient polishing.

1. Introduction

SCD has attracted great attention for its excellent application characteristics. Wide bandgap of 5.47 eV makes it a more promising semiconductor material compared with Si, GaAs and GaN [1]. Moreover, with high thermal conductivity more than 2000 W/m·K and nearly full band transmission [2], SCD also presents huge prospect in heat spreader and optical window.

Though SCD is in possession of such superior properties, its hard-to-machine nature hinders its further processing and manufacturing, especially the polishing of diamond to improve surface quality which plays a significant role in those desired fields. Mechanical polishing (MP), chemical mechanical polishing (CMP), dynamic friction polishing (DFP) and laser polishing (LP) have been proved to be accessible technologies to polish SCD [3-6], but these methods have either excessively slow MRR or excessively rough surface after treatment, far from real commercial use [7].

Herein, we propose a damage-free and ultra-smooth polishing method using high energy atmospheric pressure ICP to cope with surface quality issue of diamond, and this method is referred to as plasma-based atom selective etching (PASE). During the polishing process, oxygen is supplied as reaction gases to generate highly active oxygen atoms, selectively etching with carbon atoms in the protrusion position of diamond. Using PASE, the MRR can be increased to 33.24 μm/min and a super-smooth diamond surface with 0.667 nm *S*a roughness can be obtained. Additionally, Raman spectra results indicate that no other non-intrinsic elements and structure defects are introduced into diamond surface. PASE is believed to be a promising way to achieve atomic-scale smooth diamond surface with highly-efficient and damage-free characteristics.

2. ICP setup and plasma diagnostics

ICP setup

Atmospheric pressure ICP is a high temperature plasma with large radical density and can be obtained without sophisticated and expensive vacuum device. As shown in Fig. 1, ICP system can be divided into power supply part (radio frequency (RF) power, network matcher), gas delivery part (Ar cylinder, O_2 cylinder, gas supply lines, mass flow controllers (MFC)), plasma activation part (torch clamp, inductance coil, electric spark generator and quartz torches), numeric controller (NC) machine part (sample holder, 3-axis NC platform) and water cooling part. During the process of PASE, high temperature and high energy plasma consisting of argon and oxygen atoms would act directly on the surface of SCD, which can be selectively etched through the reaction between oxygen active particles and carbon atoms. Thorough results about the composition and real effective species in the plasma are discussed in plasma diagnostics.

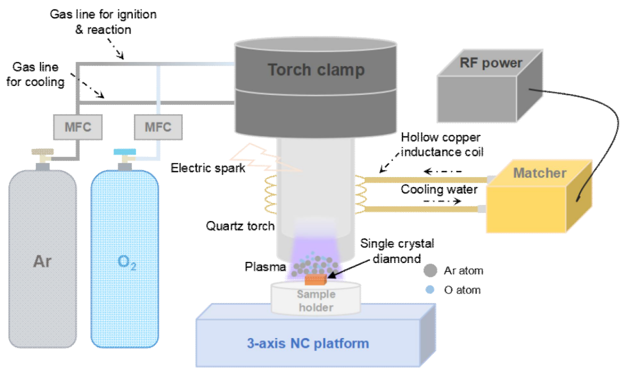

Fig. 1. Schematic of atmospheric pressure ICP setup

Plasma diagnostics

In the process of PASE, two precautions including high density of active etching particles and high etching temperature are required to achieve polishing of a rough surface of the workpiece [1]. For SCD, it is the temperature and active oxygen atoms that play the crucial role in obtaining an ultra-smooth surface. Here, diagnostics of the plasma torch in polishing SCD were conducted to investigate the species of active particles and the temperature through the experiment. Fig. 2(a) reveals optical emission spectroscopy (OES, Ocean Optics USB4000) of the plasma with and without oxygen. As we can see, there is an evident peak at the wavelength of 777.12 nm corresponding to oxygen atoms when oxygen was supplied with argon in the meantime, compared with only pure argon delivery [9]. Argon peaks dominate the wavelength from 700 to 850 nm, and it can very that oxygen atoms play a role in achieving the polishing effect combined with the intense peak of oxygen atoms at 777.12 nm. Plasma excitation image can be seen from Fig. 2(b), and the center temperature of SCD measured by an infraction imager (FLIR T660) under 1000 W plasma irradiation reaches 1377.8 ℃. These results prove that ICP can provide both reactive particles and high temperature for PASE of diamond.

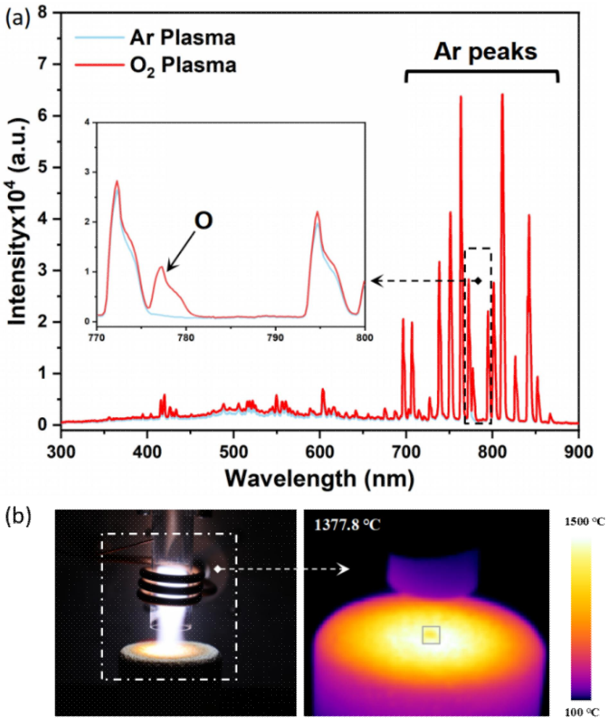

Fig. 2. Plasma excitation properties. (a) Optical emission spectroscopy of ICP, (b) Plasma excitation image and sample center temperature image

3. PASE mechanism

PASE has been successfully used to achieve high-efficiency and high-quality polishing of single crystal silicon, synthetic quartz, GaN [8, 10, 11]. It is reported that the physicochemical process of PASE is based on the fact that the surface atoms with dangling bonds are preferentially reacted with active atoms. As for SCD, carbon atoms at protrusion or defect position possess more dangling bonds which tend to react with active oxygen atoms existing in high temperature plasma, escaping from SCD surface in the form of gaseous CO_2 or CO. As a result, the atoms with more dangling bonds are removed from SCD surface and the surface carbon atoms arrange neatly, contributing to an atomic-scale smooth surface.

4. Experiment Results and Discussions

As mentioned above, the PASE experiment was conducted under 1000 W input power, obtaining high-energy oxygen active particles. To verify specific effect of PASE, SCD with many mechanical scratches and damage after MP was adopted as the initial sample. SCD was firstly irradiated under high temperature plasma and then cooled under argon atmosphere to protect SCD from oxygen etching of air. In the end, a post-treatment was used to eliminate the black non-diamond carbon layer which was produced in the process of cooling. Fig. 3 shows morphology with embedded height map of initial SCD sample and treated SCD at 1000 W for 1 min, 3 min, 5 min, 10 min and 15 min using laser scanning confocal microscope (LSCM, KEYENCE VK-X1000). Fig. 3(a) shows that several deep scratches and lots of micro defects were spread on the SCD initial surface. After only 1 min PASE treatment (Fig. 3(b)), the big scratches were much shallow and inconspicuous. As can be seen from Fig. 3(c-f), with the increase of PASE treatment time, big scratches gradually disappeared, and micro defects can not be directly detected by LSCM, manifesting that the smoothing ability of SCD through PASE treatment.

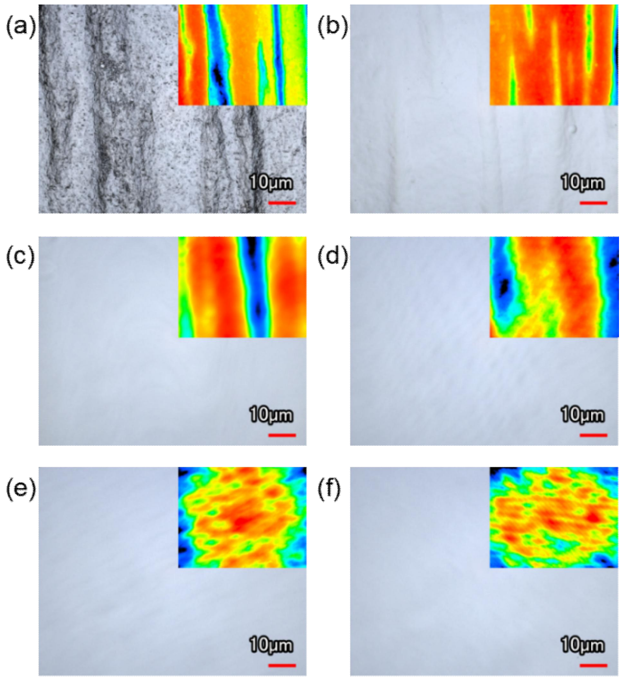

Fig. 3. Morphology of SCD under different treatment time observed by LSCM. (a) Initial rough surface, (b-f) After 1 min, 3 min, 5 min, 10 min and 15 min PASE under 1000 W, respectively

Detailed *Sa* roughness evolution and surface morphological changes during PASE treatment were obtained by use of atomic force microscope (AFM, BRUKER Dimension Edge) in tapping mode, referring to Fig. 4. As shown in Fig. 4(a-b), it is obvious that the rough initial surface of sample experienced fast selectively etching process and many etching pits gathered at the scratches sites at the beginning. Fig. 4(c-f) indicate that further plasma etching would contribute to mutual merging of etching pits and finally a rather smooth surface of SCD can be achieved. Within only 15 min, the *Sa* roughness of SCD can be reduced from 57.4 nm to 0.667 nm with MRR of 33.24 μm/min.

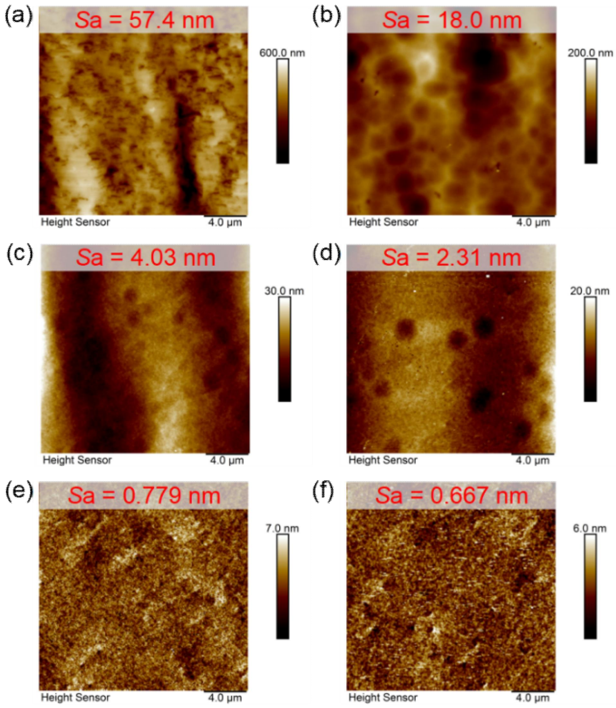

Fig. 4. *Sa* roughness evolution of SCD during PASE treatment. (a) Initial rough surface, (b-f) Different polishing duration of SCD for 1 min, 3 min, 5 min, 10 min and 15 min, respectively

Moreover, the undulating condition of a surface in the diagonal direction is revealed by Fig. 5. It can be clearly seen that the fluctuation of surface profile dropped down from 400 nm to only 6 nm in 15 min, indicating the flattening effect of PASE treatment.

Element species and surface condition of carbon material are universally characterized by Raman spectra. For the sake of analyzing whether contaminant or structure defects are introduced through PASE treatment, Raman spectra (Horiba LabRAM HR Evolution) with a 532 nm laser source were utilized to compare the characteristic peaks changes during PASE treatment process. As depicted in Fig. 6, three characteristic peaks are at the position of 1331, 1420 and 1596 cm^{-1}. The sharp and intense peak located at 1331 cm^{-1} represents diamond carbon spectrum of sp^3 hybridization while the broad and less tense peaks at 1420 and 1596 cm^{-1} refer to the $[N\text{-}V]^o$ related nitrogen impurity during the growth process of SCD and sp^2 hybridization of graphite or graphite-like carbon, respectively [12]. Nitrogen impurity can not be completely removed from diamond but its relevant intensity to diamond intrinsic sp^3 hybridization peak would decrease from 0.61 to 0.49 through PASE process, indicating PASE possesses a certain removal effect of nitrogen impurity. During the cooling process, a black non-diamond carbon layer would appear on SCD surface corresponding to 1596 cm^{-1} phonon peak which may be attributed to phase transformation of diamond to graphite or graphite-like carbon under high temperature anaerobic environment. Further post-processing would be able to eliminate the black layer and achieve pure and bright surface of SCD. Raman spectra results exhibit that PASE would not introduce any other impure elements and structure defects in the process of PASE, proving the accessibility of polishing of diamond via atmospheric pressure ICP.

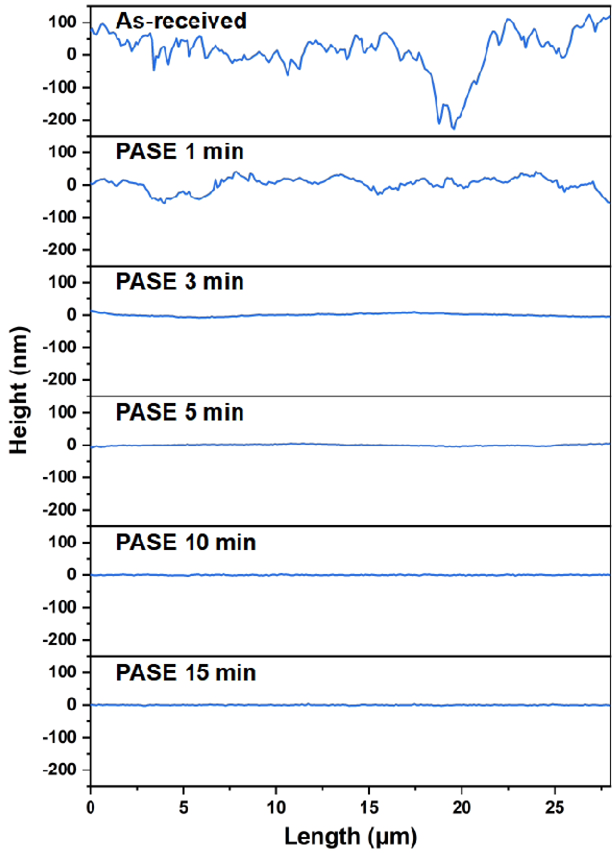

Fig. 5. Surface fluctuation profile in the diagonal direction of 20*20 μm AFM images of SCD under various PASE treatment time

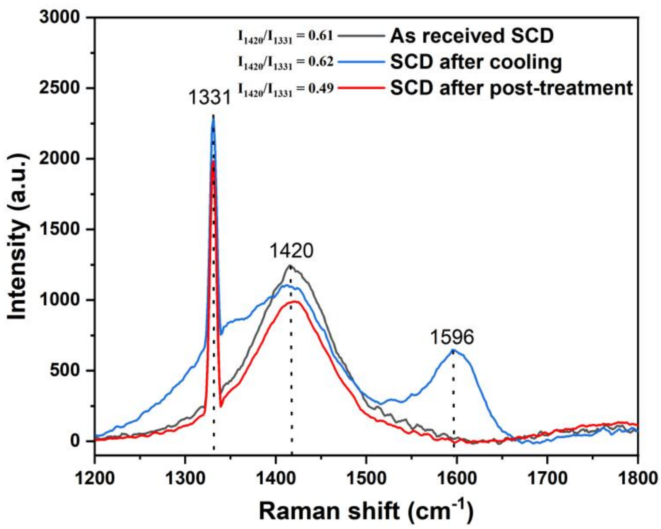

Fig. 6. Raman spectra of SCD with and without plasma treatment

5. Conclusion

In this work, SCD has been successfully polished by atmospheric pressure ICP with high-efficiency and ultra-precision. In only 15 min radiation of high temperature plasma at 1000 W, SCD can be evolved from a initial rough surface having considerate mechanical scratches to an ultra-smooth surface, with the corresponding *S*a roughness decreasing from 57.4 to 0.667 nm. Moreover, the MRR is up to 32.24 μm/min, which is thousands times of conventional polishing methods. Raman spectra further verify that non-intrinsic impurity and structure defects would not be introduced by PASE process. Overall, PASE polishing method goes far beyond the polishing techniques of SCD reported before in terms of efficiency and surface roughness, being a promising solution to achieve atomic-smoothness SCD surface with impressive MRR.

6. References

[1] C. J. Wort, R. S. Balmer, Materials Today, 11 (2008).

[2] C. J. Wort, C. S. J. Pickles, A. C. Beale, C. G. Sweeney, M. R. McClymont, R. J. Saunders, R. S. Sussmann and K. L. Lewis, Window and Dome Technologies and Materials VI, 3705 (1999).

[3] A. Kubota, S. Nagae and S. Motoyama, Diamond and Related Materials, 101 (2020).

[4] S. Yuan, X. Guo, J. Huang, M. Lu, Z. Jin, R. Kang, and D. Guo, Diamond and related materials, 100 (2019).

[5] H. Xu, J. Zang, G. Yang, S. Jia, P. Tian, Y. Zhang, Y. Wang, Y. Yu, J. Lu, X. Xu and P. Zhang, Diamond and Related Materials, 80 (2017).

[6] H. Liu, L. Xie, W. Lin and M. Hong, Advanced Optical Materials, 9 (2021).

[7] H. Yang, Z. Jin, L. Niu, H. Wang and H. Niu, Diamond and Related Materials, 125 (2022).

[8] Z. Fang, Y. Zhang, R. Li, Y. Liang and H. Deng, International Journal of Machine Tools and Manufacture, 159 (2020).

[9] H. Luo, K. M. Ajmal, W. Liu, K. Yamamura and H. Deng, Carbon, 182 (2021).

[10] R. Li, Y. Zhang, Y. Zhang, W. Liu, Y. Li and H. Deng, Journal of Manufacturing Processes, 60 (2020).

[11] L. Zhang, B. Wu, Y. Zhang and H. Deng, Applied Surface Science, 620 (2023).

[12] K. Beha, A. Batalov, N. B. Manson, R. Bratschitsch and A. Leitenstorfer, Physical Review Letters, 109 (2012).