High-efficiency smoothing of polycrystalline diamond via plasma-based atom-selective etching

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Abstract. Due to the extreme mechanical hardness and chemical inertness, the smoothing of polycrystalline diamond (PCD) posses various challenges, such as a low material removal rate, excessive damage introduction, and difficulty in achieving sub-nanometer roughness. These issues greatly impede the further industrial applications of PCD. Herein, we propose using atmospheric inductively coupled plasma for smoothing PCD based on plasma-based atom-selective etching. This method has been proven to achieve high-efficiency smoothing of PCD without introducing new damage. During the etching process, oxygen is added to argon plasma to generate highly reactive oxygen radicals. These radicals can etch the carbon atoms on diamond surface with different rates according to their atomic bonding states, reducing the *S*a roughness of PCD from 301 nm to 20.6 nm in only 30 minutes. The material removal rate of PCD can be as high as tens of micrometers per minute, thousands of times higher than conventional mechanical/chemical mechanical polishing methods. Furthermore, X-ray diffraction spectra and Raman spectra results indicate that no amorphous carbon or new stress is introduced, and the crystal structure remains consistent before and after smoothing. Hence, combined with chemical mechanical polishing and other fine polishing methods, plasma-based atom-selective etching is believed to serve as an efficient pre-polishing approach to significantly increase the overall polishing efficiency of PCD.

1. Introduction

Diamond is one of the most precious mineral materials, with strong carbon-carbon covalent bond hybridizing in sp^3 form, and the bond energy can be as high as 347.5 kJ/mol, resulting in its extreme chemical inertness. Moreover, the distinct bonding character and crystal structure make diamond posses superior properties, such as a high thermal conductivity of 2200 W/m·K, an excellent bandgap with 5.47 eV [1], a perfect light transmittance in nearly full waveband, and a HV hardness as high as 100 GPa [2]. Combined with the outstanding features [3-5], diamond can be widely used as heat spreader, semi-conductor, optical window, and wear-resistant coating materials.

Nowadays, due to the exorbitant production cost, immature growth technique, and difficulty in obtaining large-size wafer, high-quality single crystal diamond is still hard to meet the application requirement of the industry. Therefore, polycrystalline diamond (PCD) has become the mainstream of market by virtue of the lower cost of production, larger size, and similar performance. However, dislocation, twin structure, and holes are apt be introduced in PCD for its competitive growth process. Meanwhile, there are various grains randomly distributing on the original surface of PCD and it's difficult to obtain high-quality surface to fulfill the application demand in the industry. On the other hand, the strong chemical inertness and extreme hardness also make PCD a typical difficult-to-machine material, which contributes to the introduction of undesirable scratches, pits, amorphous layer on PCD in the process of conventional mechanical polishing [6]. What's more, though chemical mechanical polishing can combine chemical modification and mechanical shear removal to reduce the *S*a roughness to lower than 3 nm in more mild conditions, the time-wasting polishing process is unacceptable, inhibiting the further practical application of PCD [7, 8].

In this study, smoothing of PCD on the principle of plasma-based atom-selective etching (PASE) is proved to be a highly efficient pre-polishing approach to significantly improve the overall polishing efficiency of PCD. During the smoothing process, oxygen is adopted as reaction gas in atmospheric inductively coupled plasma (ICP) to generate highly active oxygen radicals, selectively etching carbon atoms with different etching rates on the surface of PCD, decreasing the *S*a roughness of PCD from 301 nm to 20.6 nm in 30 minutes. The material removal rate (MRR) can reach up to 34.4 μm/min, which is thousand of times that of conventional mechanical/chemical mechanical polishing methods. In addition, X-ray diffraction (XRD) spectra and Raman spectra analysis confirm that the final surface of PCD is free of non-diamond carbon, exhibit no newly introduced stress, and retain a consistent crystal structure before and after smoothing. Therefore, by applying PASE as a pre-polishing process, it's promising to smooth PCD with both high efficiency and low roughness.

2. Experiment details

2.1 Experimental materials and setup

PCD samples used in this study are fabricated through DC Arc Plasma Jet chemical vapor deposition with a dimension of 3 × 3 × 1 mm^3. The initial surface of PCD consists of randomly distributed grains and all PCD samples are washed in anhydrous ethanol and pure water, respectively. Argon and oxygen with a purity higher than 99.999% are used as plasma gas source.

As shown in Fig. 1, atmospheric ICP setup is mainly composed of five parts, including plasma working zone (torch clamp, inductance coil, and coaxial quartz torches), radio frequency (RF) power supply, electric sparker, RF match, mass flow controller, and water cooler. During the smoothing process, argon is introduced into the outer tube as cooling gas and into the inner tube as as carrier gas. Oxygen is also introduced into the inner tube and play a role of reaction gas to generate reactive radicals.

Fig. 1. Atmospheric ICP setup.

2.2 Plasma diagnostics

Fig. 2 demonstrates the excitation properties of ICP. It is obvious that there is a distinct peak of oxygen radical located at 777.3 nm for the optical emission spectrum of oxygen plasma in Fig. 2(a), while there is no such a peak for pure argon plasma. Despite this significant difference, the optical emission spectra of oxygen plasma and argon plasma almost overlap in the wavelength range of 200 to 850 nm, with the characteristic peaks of Ar nearly occupying the whole wavelength range. The added oxygen is ionized in the atmosphere of Ar plasma and generates highly reactive oxygen radicals. Fig. 2(b) shows the temperature profile of PCD surface when exposed to oxygen plasma at 1200 W RF power. The surface temperature of PCD can quickly rise to 1300 °C within 20 s, then gradually increase until it reaches a thermal equilibrium, eventually stabilizing around 1500.2 °C. Once the smoothing process finishes and the plasma setup is shut down, the surface temperature of PCD would experience a quick decrease.

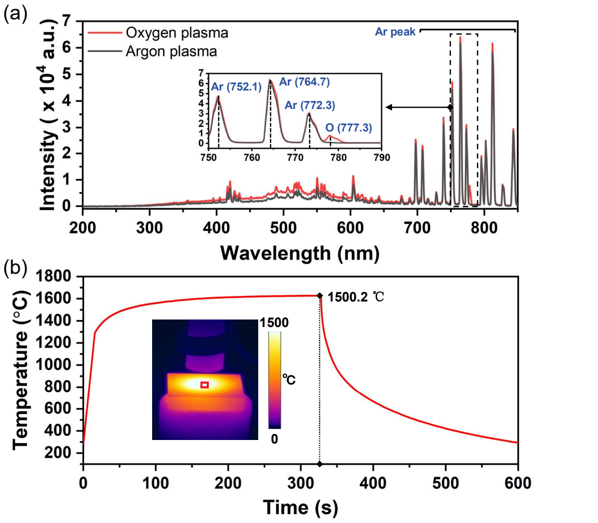

Fig. 2. Plasma excitation properties. (a) Optical emission spectroscopy of ICP. (b) Temperature profile of PCD under the irradiation of oxygen plasma.

2.3 Mechanism of PASE

The smoothing process of PCD is based on the principle of PASE, where carbon atoms are efficiently removed with varying rates according to its bonding state. Specifically, the initial surface of PCD is rather rough with a haphazard distribution of carbon atoms. When the surface of PCD is fully exposed to oxygen plasma, the carbon atoms obtain sufficient activation energy and are absorbed by reactive oxygen atoms [9]. Since carbon atoms at the protrusion of diamond grain are only connected to the carbon atoms in the lower layer, they tend to have fewer bonds and lower reaction activation energy compared with the carbon atoms at the base layer. Consequently, the highly reactive oxygen atoms would react with these carbon atoms preferentially and form CO/CO_2, resulting in the selective removal of carbon atoms. As a result, the protrusion on the surface of PCD are quickly removed and the surface height difference decreases rapidly, contributing to a smooth surface.

3. Results and discussion

3.1 Smoothing Results

Fig. 3 shows surface morphology of PCD before and after smoothing. In Fig. 3(a), it is can be clearly seen that the initial surface of PCD is extremely rough, the surface morphology is severely undulating, and the grain structure is sharp and angular. Fig.3 (c) demonstrates the initial surface of PCD in a smaller scale. Various grains stick to each other without any order and there are many deep gaps between them, causing a high *S*a roughness of 301 nm. However, after smoothing for 30 min, the protrusion and huge height difference of PCD disappear, which is shown in Fig. 3(b). Also, plenty of sharp and angular grain structure are eliminated, and it is hard to distinguish the boundary of two grains. Though there are still some undulating grain boundary zones on the surface, the surface quality of PCD has been significantly improved. Meanwhile, the *S*a roughness of PCD decreases to 20.6 nm, as shown in Fig. 3(d). It is worth noting that the relatively high roughness is mainly caused by some grain boundaries. For example, the *S*a roughness of the grain boundary-free regions A (3 μm × 3 μm) and C (3 μm × 3 μm) is 3.23 nm and 3.36 nm, respectively. However, the *S*a roughness of the grain boundary region B (3 μm × 3 μm) and D (3 μm × 3 μm) reach 33.7 and 16.6 nm, respectively. The difficulty in smoothing grain zones may arise from the complex arrangements and bonding states of carbon atoms.

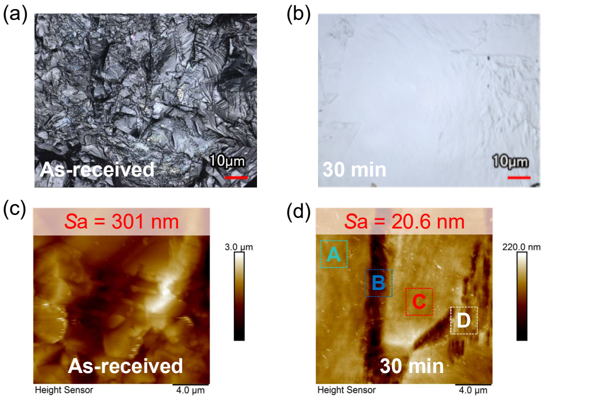

Fig. 3. Surface morphology of PCD in different measuring scale. Initial surface of PCD at the large (a) and small (c) scale. Surface morphology of PCD after smoothing for 30 min at the large (b) and small (d) scale.

3.2 MRR evolution results

The smoothing of PCD through PASE demonstrates a remarkably high MRR, as shown in Fig. 4. At the beginning of smoothing process, the MRR can be as high as 44.3 μm/min. As the smoothing process continues, the MRR decreases dramatically to 37.6 μm/min within 2 minutes, and then the downtrend slows down until 20 minutes, when the MRR stabilizes at around 34.4 μm/min.

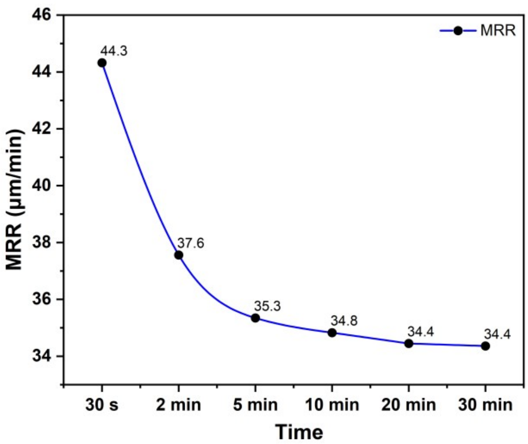

Fig. 4. MRR evolution of PCD during the 30 min smoothing process.

During the initial smoothing stage of PCD, PCD possesses a rather rough surface, with randomly distributed grains and significant height difference between them. When PCD is exposed to oxygen plasma irradiation, carbon atoms at the tips of the grains are preferentially etched, and the entire reaction area gradually declined as the grain tips are removed, leading to a decrease in MRR. After 20 minutes of smoothing, the whole surface of PCD becomes flat, and the bonding states of the majority of carbon atoms on the surface reach equilibrium. As a result, the etching rate of the carbon atoms on PCD surface comes into stabilization, resulting in a stable MRR.

3.3 Analyses of surface composition

The composition and residual stress of PCD before and after smoothing are analyzed using Raman spectra. As shown in Fig. 5, the measurement range is from 1000 to 2000 cm^{-1}. The as-received PCD is in its initial condition and there is a characteristic sp^3 hybrid peak of diamond located at 1331.5 cm^{-1}, which is slightly offset from the characteristic peak at 1332.5 cm^{-1} of typical IIa diamond [10]. This small offset may arise from the residual stress in PCD. According to the relationship between residual stress and the offset, namely, $\sigma = -0.567 \times \delta v$ [11], the residual stress in PCD can be concluded to be tensile with a vaule of 0.567 GPa. Here, σ represents the residual stress and $\delta v = v - 1332.5$ cm^{-1}, while v is the measured wavenumber of characteristic peak of PCD. The tensile stress mainly originates from the competitive growth of grains. A broad peak adjacent to the characteristic peak may arise from sp^2 defect or nitrogen impurity inside PCD [12]. After smoothing, there is no offset for the characteristic peak of PCD, indicating that no new stress was introduced during this process, which is a remarkable advantage of smoothing through PASE. Additionally, no other non-diamond peaks are present in the measurement range, confirming that the use of oxygen plasma smoothing does not introduce non-diamond carbon or alter the intrinsic structure of PCD.

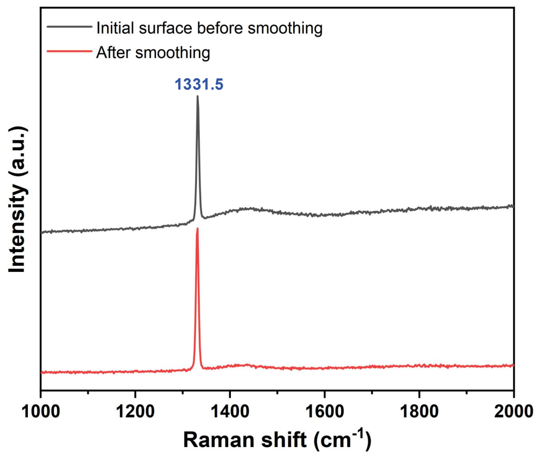

Fig. 5. Raman spectra of PCD before and after smoothing.

The orientation of grains in PCD is further analyzed by X-ray diffraction spectra. As shown in Fig.6, the orientation of grains remains unchanged before and after smoothing, with the (111) crystal plane located at 44.12°, the (220) crystal plane at 75.47°, the (311) crystal plane at 91.64°, and the (400) crystal plane at 119.63° [13]. Among these crystal planes, the characteristic peak intensity of the (220) crystal plane is dominant all the time, followed by the (111) crystal plane, while the intensity of the (400) crystal plane is relatively low, indicating that this crystal plane has a very small component on the surface of PCD. Additionally, during the smoothing process, although the MRR of PCD remains high, the orientation of grains shows no significant change. This phenomenon demonstrates that PASE acts on all crystal planes of PCD without preference for any specific crystal plane. The etching rate of carbon atoms in PCD does not depend on the crystal plane but rather the bonding states. When the bonding states are inconsistent, highly reactive oxygen radicals preferentially react with carbon atoms that have fewer C-C bonds. As a result, the bonding states of carbon atoms gradually change, and eventually, all carbon atoms on the surface of PCD tend to become consistent, leading to a smooth PCD surface.

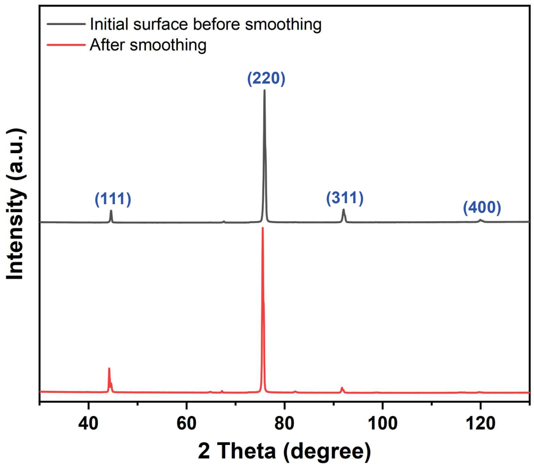

Fig. 6. XRD spectra of PCD before and after smoothing.

4. Conclusions

Atmospheric inductively coupled plasma has been shown to successfully smooth PCD with high efficiency, based on the principle of PASE. As a high-efficiency smoothing method, it can be used as a pre-polishing process to significantly improve the surface state of PCD, greatly shortening the overall polishing duration. The conclusions from the experiment results are as follows:

(1) The oxygen plasma contains highly reactive oxygen radicals, which generate an atom-selective etching effect on the surface of PCD. Carbon atoms with fewer C-C bonds are preferentially removed, resulting in a smooth PCD surface.

(2) During the smoothing process, the *S*a roughness of PCD is reduced from 301 to 20.6 nm in just 30 minutes, with no need for any pre-treatment steps.

(3) Throughout the smoothing process, the MRR of PCD decreases rapidly first, and then the downward trend slows down, with the MRR finally stabilizing at around 34.4 μm/min, demonstrating the high-efficiency smoothing of PCD.

(4) Comprehensive analysis of surface composition and crystal structure of PCD indicates that the smoothing of PCD through oxygen plasma does not introduce any non-diamond carbon on the surface of PCD, nor does it increase the tensile stress or alter the grain orientations for PCD.

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