Plasma-etching Enhanced Dynamic Friction Polishing for Single Crystal Diamond Films

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***Abstract*—In view of the high time-consuming and inefficiency polishing of diamond, this paper uses inductively coupled plasma (ICP) etching technology to treat the surface of single crystal diamond, and then obtains an ultra-smooth surface with the roughness as low as 0.39 nm over 100 μ m^2 through dynamic friction polishing (DFP). The material removal principle is confirmed by the test results of atomic force microscope (AFM) and X-ray photoelectron spectroscop (XPS), the surface of the etched diamond has a direct phase transformation from crystalline to amorphous carbon, greatly improving the subsequent polishing rate and quality. It is of great significance to realize the high-level industrialization of diamond.**

Keywords—Diamond, ICP etching, DFP

I. Introduction

With the rapid development of the semiconductor industry, there is an increasing demand in the industry for high-power electronic devices with high temperature resistance and high voltage resistance. In addition, as Moore's Law has gradually approached its limit, resulting in further improvement of miniaturization and integration of devices. For the current high-power devices, ineffective heat dissipation limits its performance. Therefore, diamond [1-3], a fourth-generation semiconductor material with a large band gap (5.47 eV), excellent chemical stability and known as the highest thermal conductivity (2000-2320 W/mK), has attracted more and more attention.

The successful development of synthetic diamond [4-5] has led to significant advancements and applications in various fields. However, for industrial development, how to efficiently obtain high-purity diamond surfaces has become a problem that restricts the further development of diamond materials. Therefore, a high quality and high efficiency diamond polishing technology is essential.

Watanabe et al proposed a new process for ultraviolet radiation polishing of diamond [6], which combined chemical mechanical polishing (CMP) with UV-induced photochemical reaction. By using UV light with a wavelength range of 200-400 nm, the carbon atoms on the diamond surface are oxidized by active substances such as hydroxyl radicals and oxygen radicals at localized high temperatures, and then removed in the form of CO and CO_2. The material removal rate (MRR) of this polishing method is 0.5 mm/h, which is 1.7 times than that non-ultraviolet irradiation; K. Yamamura et al [7] utilized Ar-based plasma assisted polishing technology with water vapor to polish the single crystal diamonds deposited by chemical gas, obtaining a diamond surface without residual stress, with MRR value of 2.1 mm/h; Yuan et al [8] made a FeNiCr alloy polishing plate by combining hot pressure sintering and mechanical alloying, and used this alloy polishing plate to tribochemical polish (TCP) the artificially grown diamond film. This method can make the diamond interact with the polishing plate through friction, and convert it into amorphous carbon for removal. Ultimately, they obtained the material removal rate of 3.7 mm/h. However, Raman analysis revealed that compressive residual stress still exists on the polished diamond surface after polishing in this way.

Currently, a variety of polishing methods for diamond materials are available, whether by physical removal or chemical removal; with or without abrasive; contact [9] or non-contact [10] have their own advantages and drawbacks. For carbon materials, different crystal structures result in different physical and chemical properties among their allotropes. Therefore, the diamond surface can be polished by converting it into graphite with minimal intermolecular force. Inductively coupled plasma etching technology is an effectively experimental approach to using diamond graphitization to flatten its surface at high speed [11-12]. Except for efficiently obtaining high-quality diamond surfaces, compared with the traditional diamond polishing technology, this approach offers a simpler experimental environment, without high temperature heating devices and other vacuum-sealed environments.

The processes flow for ICP etching and DFP of single crystal diamond (SCD) are given in Section II. Under the bombardment of plasma, the crystal lattice structure of diamond is disrupted, and a large amount of amorphous carbon is produced on its surface, which is subsequently removed through dynamic friction polishing. Based on the principle analysis mentioned above, the changes of diamond surface are observed and detected by AFM and XPS in Section III. In the end, a high cleanliness surface with an Ra of about 0.39 nm was obtained over the test area of 10 μm*10 μm. It provides a promising solution to simplify diamond polishing environment and improve diamond polishing rates.

II. Experimental procedure

In this study, diamond surface was treated by ICP etching first, followed by DFP to achieve an ultra -smooth surface.

A. ICP etching experiment

ICP etching changes the surface through plasma physical bombardment and chemical reactions. ICP devices consist of two independent RF power sources, RF1 and RF2. The electrodes outside the chamber generate an alternating magnetic field inside, and when the field is strong enough, the gas will enter the plasma state. The path of charged ions in the plasma changes with the electrode voltage outside the chamber. The voltage on the electrodes inside the chamber

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provides energy to the plasma. The main mechanisms of ICP etching are shown in Figure 1. Physical etching is the impact of plasma colliding with the surface of the diamond samples, which destroys the originally stable structures. The C-C covalent bond breaks under the bombardment of plasma, which belongs to isotropic etching. In chemical etching, the etching gas undergoes inductively coupled plasma discharge to generate plasma. so the plasma reacts with the substrate surface anisotropy in a specific direction under the influence of the electric field.

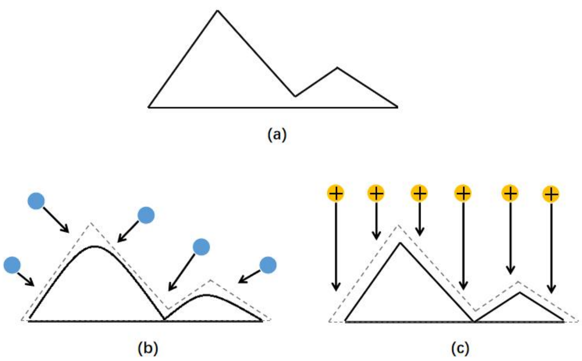

Fig. 1. (a) Initial diamond surface, (b) Surface after isotropic etched, (c) Surface after anisotropic etched.

As a carbon-based material, diamond is typically etched by using oxygen [13] as the etching gas. Under the action of inductance coupling, oxygen forms oxygen plasma, part of which chemically reacts with carbon atoms on the diamond surface to produce gases such as carbon monoxide and carbon dioxide. These gases volatilize from inside the device under the action of air flow to remove materials; in the other part, high-speed bombardment through physical action destroys the stable tetrahedral structure of sp^3 carbon atoms, and looses the lattice structure, which is then converted into more easily removable amorphous carbon [14], and improves efficiency in subsequent polishing.

The ICP etching parameters for this experiment are set to the upper electrode 100 W, the lower electrode 100 W, with an oxygen flow of 50 sccm.

B. DFP experiment

Figure 2. shows a schematic diagram of the experimental device for dynamic friction polishing. During the polishing process, the abrasive in the polishing fluid will destroy the diamond surface atomic layer under the action of pressure, and together with the high temperature generated by friction, the diamond will be transformed into the graphite phase, and then the amorphous carbon generated on the surface will be removed, resulting in a high and smooth clean surface. The greater the hardness of the abrasive, the stronger the polishing pressure and mechanical action effect on the substrate surface. Because diamond is the hardest material in nature, diamond abrasives are used for the polishing liquid in this experiment.

The DFP experiment is configured with a polishing control instrument weighing 2100 g, each of the four weights weighing 100 g, and is conducted at a rotational speed of 45 rpm. Frosted leather is used as polishing disc material. In this experiment, according to diamond surface roughness, the X03-0520D4 type polishing liquid is selected. Since the diamond size in this experiment is 0.7 cm*0.7 cm, the pressure on the sample surface during the DFP experiment is about 0.51 MPa.

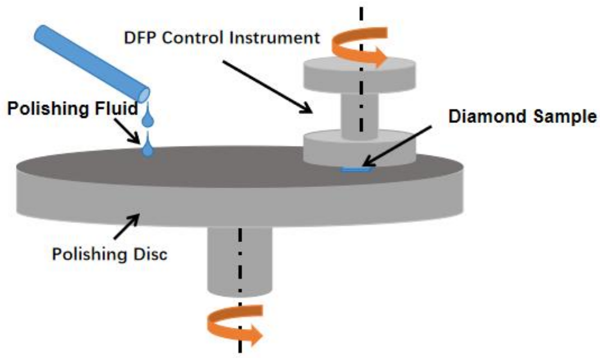

Fig. 2. Schematic diagram of the experimental device for DFP experiment.

Under the experimental parameters mentioned above, ICP etching was conduced on the surface of the diamond sample for 7 min. In order to investigate the influence of plasma etching on diamond polishing, two kinds of samples with and without plasma etching were prepared. The etched sample is recorded as SCD1, and the unetched sample is SCD2. After a 12-hour DFP experiment, the diamond samples undergoes a 1-hour acid wash at 130 ℃ , and the proportion of concentrated sulfuric acid to hydrogen peroxide in the mixed solution is 3:1.

III. TESTING AND CHARACTERIZATION OF SINGLE CRYSTAL DIAMOND POLISHED SURFACE

A. AFM analysis of single crystal diamond polished surface

To investigate the changes of diamond surface roughness during the experiment, AFM (Bruker Dimension FastScan) was used to test the roughness of initial surface， plasma etched surface and polished surface. Figure 3. and Figure 4. show the AFM images of SD1 and SD2, respectively.

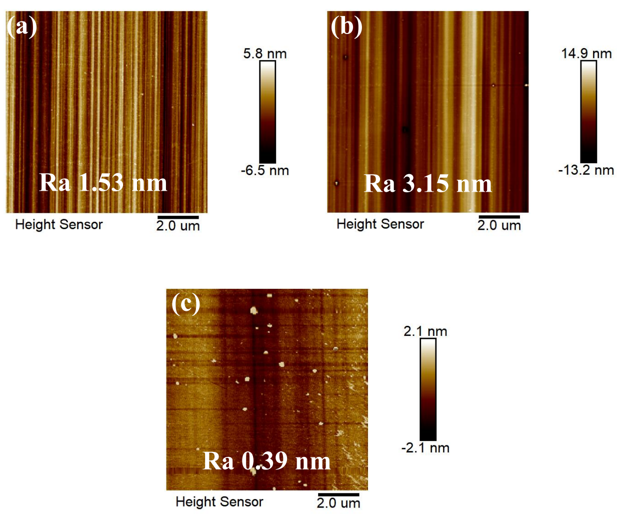

Fig. 3. AFM images of SD1 diamond surface. (a) Initial surface, (b) Plasma etched surface, (c) Polished surface.

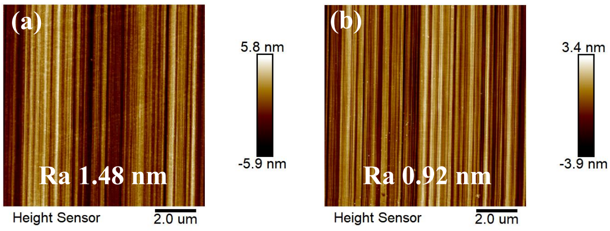

Fig. 4. AFM images of SD2 diamond surface. (a) Initial surface, (b) Polished surface.

The evolution of AFM data from SCD1 and SCD2 reveal that the surface roughness of the diamond sample SCD1 increased from an initial 1.53 nm to 3.15 nm after ICP etching. This is because the initial roughness of the sample itself was relatively low, and the surface is relatively flat. And the plasma bombardment will produce amorphous carbon and other substances on the originally smooth surface, resulting in an increase in its roughness after etching. However, after dynamic friction polishing, SCD1 finally obtained an ultra-smooth surface with an Ra value of 0.39 nm. Conversely, the surface roughness of the sample SCD2 was decreased from 1.48 nm to 0.92 nm which is much higher than SCD1. This is because in the ICP etching process, the rough protrusions parts of the diamond surface were more likely to be bombarded by oxygen plasma. Part of them generate volatile gases such as CO_2 and CO, and another part gathers a large amount of amorphous carbon in these areas due to surface tension. Thus, due to the generated amorphous carbon in the interface, the roughness of diamond can be decreased at a faster rate [15] in the subsequent DFP process, rapidly achieving a flat surface on the etched diamond sample. In contrast, SCD2 sample has a surface composed of hard sp^3 carbon, resulting in a lower polishing rate. The above results indicate that under the combined action of plasma etching and DFP, the diamond sample can achieve higher quality surface in a shorter time.

Additionally, to visually represent the changes in surface roughness of SCD1 and SCD2 during the polishing process, theroughness variation rate curves for the samples were shown in Figure 5.. It can be seen that the surface roughness of SCD1 samples decreased rapidly in the early stage of polishing experiment, which was much higher than that of the SCD2 sample. However, with the polishing experiment progresses, its roughness variation rate gradually decreases, and eventually approaches that of the unetched sample group. In the DFP experiment, Ra decreased rapidly in the early stage was due to that during polishing stage, the friction between the abrasive and sample would preferentially remove the convex part. At this time, the contact area between abrasive and sample is small, the polishing pressure is strong, and the surface of the etched diamond sample is mostly graphite, which is easier to remove. Therefore, the polishing rate is high, which is consistent with the material removal mechanism mentioned above. Then, with the polishing experiment, the peaks of the convex part gradually flatten out, resulting in a gradual increase of the abrasive and its contact area, a decrease in contact pressure, and a rapid decrease in the graphite content generated by etching. So in the later period， the roughness variation rate decreases progressively until it becomes relatively constant.

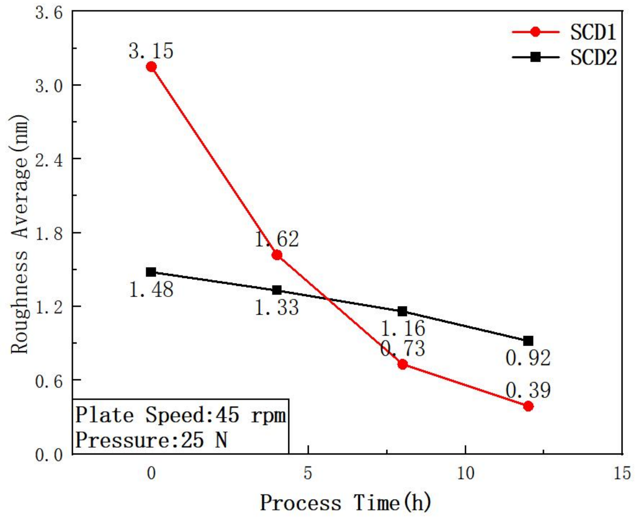

Fig. 5. SCD1 and SCD2 roughness variation rate curves.

B. XPS analysis of single crystal diamond polished surface

XPS was used to further determine the structure and chemical bond evolution of the diamond sample surface at each stage of the experiment [16-17]. All peak fittings in this experiment were conducted using the "advantage" software, and the diamond C-C peak with an energy of 284.8 eV [18] is calibrated to analyze the surface before and after ICP etching.

Figure 6. and Figure 7. depict the deconvolution O 1s and C 1s XPS spectra of the SCD1 in the pure oxygen plasma environment, respectively. Figure 6. shows the O 1s peak fitting before and after the ICP etching experiment. It can be clearly seen from the graph that the content of the C-O bonds increases significantly after ICP etching. This indicates that during the etching process, a part of oxygen atoms introduced react with the carbon on the diamond surface, forming gases such as CO and CO_2, while another part remains on the diamond surface in the form of carbon oxides.

It can be seen from the Figure 7.(a) that there is a small amount of sp^2 graphite phase corresponding to 283.64eV peak on the original surface of diamond. After the oxygen plasma etching, the integrated area of sp^2 carbon peak at 283.64 eV is increased, as shown in Figure 7.(b). Since amorphous carbon is a mixture of sp^2 graphite phase and sp^3 diamond phase, the results of the XPS peaking fitting diagram indicate that after the plasma etching, the amorphous carbon will be generated on the diamond surface, and after the DFP experiment, the structure with weaker interatomic forces will be further removed. As a result, the diamond ultimately achieves a stable, high clean and damage-free surface

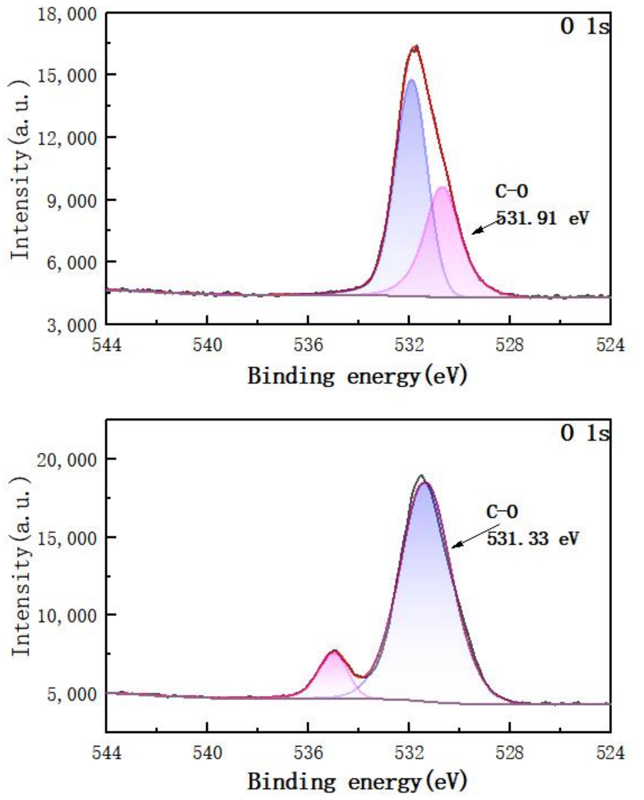

Fig. 6. Fine fitted O 1s XPS spectra of SCD1. (a) Initial surface, (b) Etched surface.

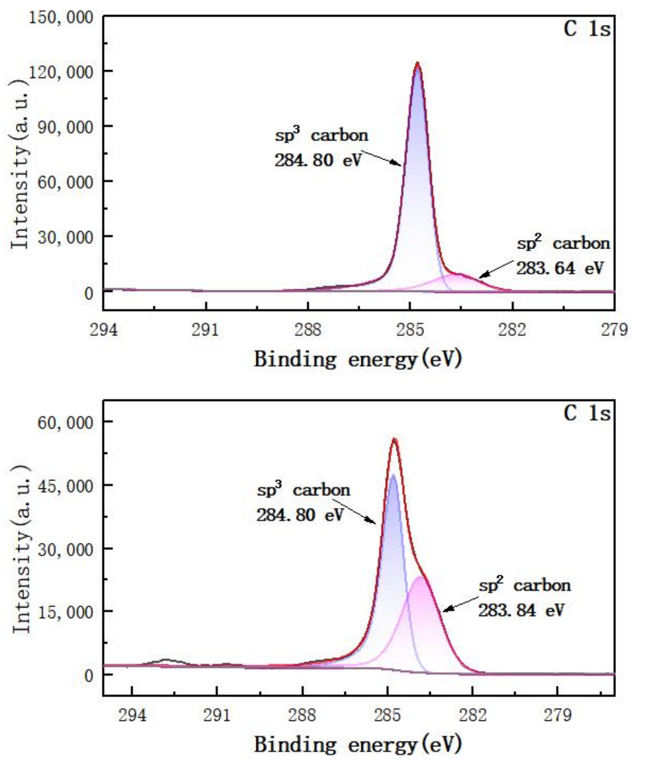

Fig. 7. Fine fitted C 1s XPS spectra of SCD1. (a) Initial surface, (b) Etched surface.

TABLE I. THE CONTENT CHANGES OF C-O BOND AND SP^2 GRAPHITE PHASE IN XPS SPECTRA BEFORE AND AFTER ICP ETCHING

Peak area	***Initial surface***	***Plasma etched surface***
C-O bond	10472	37201
Sp^2 graphite phase	17396	43612

IV. CONCLUSIONU

In this paper, the single crystal diamond surface was polished by combining ICP and DFP, and finally, we obtained a low roughness surface. The roughness of diamond was characterized by AFM, and the mechanism of plasma etching to improve polishing was confirmed by XPS. The experiment results suggested that a large amount of amorphous carbon was produced on the diamond surface under the bombardment of plasma during the etching process, and this part was effectively and rapidly removed during the subsequent polishing process. Thus, this resulted in an improvement in the surface quality of the diamond. This method offers high surface accuracy, simple operating environment and process, greatly reducing the difficulty and costs of polishing, simplifying equipment requirements, which is highly conducive to the future industrialization development. It will be an important technology for achieving high-speed, high-quality polishing of diamonds and promoting the application and development of diamond industries.

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