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Evaluation research of polishing methods for large area diamond films produced by chemical vapor deposition

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Abstract

The current study compared several polishing techniques of chemical vapor deposition (CVD) diamond films. Although research on various diamond polishing techniques has been carried for years, some issues still need to be examined in order to facilitate application on large areas in a cost-efficient manner. In the present work, microwave plasma enhanced chemical vapor deposition (CVD) was used to obtain diamond films with full width half magnitude (FWHM) less than 10 wavenumbers at 1332 cm^{-1} Raman peak. The diamond films were processed through mechanical polishing, chemical-assisted mechanical polishing, thermo-chemical polishing, excimer laser ablation, and catalytic reaction assisted grinding. A profilometer, an atomic force microscope, and a scanning electron microscope have been used to evaluate the surface morphology of diamond films before and after polishing. The results obtained by using the above mentioned techniques were analyzed and compared.

Keywords: Diamond film polishing; Chemical-assisted mechanical polishing; Catalytic reaction assisted grinding; Thermo-chemical polishing

1. Introduction

Industrial synthetic diamond has excellent physical and chemical properties. It ranks the highest in terms of hardness (ca. 90 GPa), compression strength (1.2×10^{12} N m^{-2}), coefficient of thermal conductivity (2×10^{3} W m^{-1} K^{-1}), and acoustic wave speed (17.5 km s^{-1}). In 1970, Derjaguin and Fedoseev [1] discovered how to produce synthetic diamond by using chemical vapor deposition method. Since then, large area substrates have been used to produce CVD diamond and many applications of CVD diamond have been investigated [2–4]. Today, it is used extensively in traditional cutting tools and grinding materials in order to increase the cycle time [5,6]. In recent years, the advancement of CVD technology has extended the industrial applications of CVD diamond, which is now used in high-frequency communications, opto-electronic devices, and diamond semiconductors.

Although CVD diamond film has many outstanding properties, the film has a non-uniform thickness, a non-uniform grain size, randomly oriented crystals, and a high surface roughness. In addition, the CVD diamond films are of different quality, and this highly influences the machinability and the processing time. These characteristics unfortunately limit the application of CVD diamond films in recent commercial technology. Although numerous machining methods [7–21] have been explored over the years, including mechanical polishing, chemical-assisted mechanical polishing, thermo-chemical polishing, laser ablation, ECR plasma polishing and catalytic reaction assisted grinding, it is necessary to further explore how these techniques can be perfected to facilitate processing larger areas of diamond films at a lower cost for commercial application. Based on the above mentioned information, the current study compares several polishing techniques on identical CVD diamond films.

2. Experimental methods

In the current study, five separate experiments using different methods, including mechanical polishing, chemical-assisted mechanical polishing, thermo-chemical polishing, excimer laser

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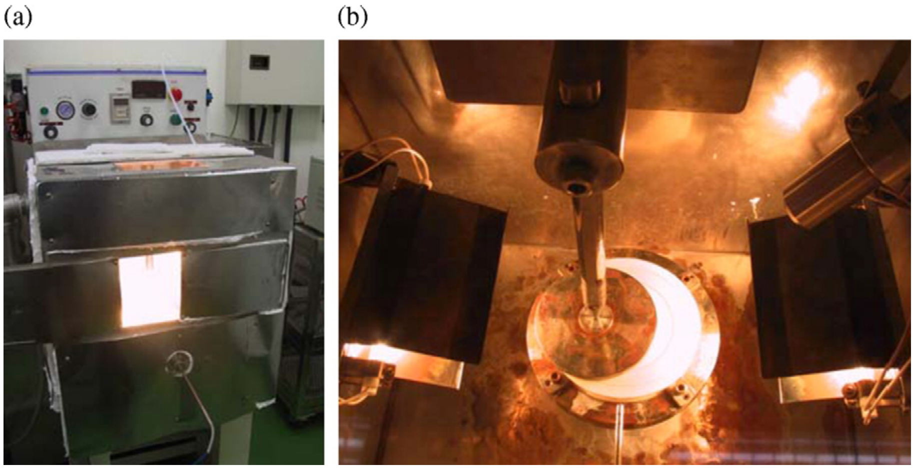


Fig. 1. Equipment photos of chemical-assisted mechanical polishing method. (a) The polishing CVD diamond film apparatus; and (b) the working chamber while polishing.

ablation and catalytic reaction assisted grinding, were carried out on five identical CVD diamond film samples for comparative purposes.

2.1. Deposition of diamond films

The quality and orientation of diamond film are influenced by several parameters including temperature, pressure, deposited position and deposition time [22–24]. In the current study, the microwave power was controlled at 15–60 kW with the (H_2–CH_4) gas system, methane concentration was kept within a range of 2 to 4% in total gas flow, while the pressure in the reactor was maintained within the range of 120–160 mbar. Diamond films were grown on (100) silicon wafers with a 5 mm thickness. Thick silicon was used to prevent any bending and deformation that would result from the high temperatures required in this process. In general, diamond powder scratch method is the pre-treatment process of silicon substrates for the following deposition [25].

2.2. Treatments

The samples were processed through mechanical polishing, chemical-assisted mechanical polishing, thermo-chemical polishing, excimer laser ablation and catalytic reaction assisted grinding methods.

2.2.1. Mechanical polishing and chemical-assisted mechanical polishing

The chemical-assisted mechanical polishing method is referred to in a paper by W.D. Brown [13]. The traditional polishing machine was modified and the metal plate was replaced by a ceramic plate with concentric circle grooves on it. In addition, infrared lamps were used in the heating system, and the processing temperature was kept at 350 °C by PID control system. The CVD diamond film sample was held by a stainless steel holder, which rotates and swings when the sample comes into contact with the ceramic plate during machining. The schematic diagram of the machine used in the current study is shown in Fig. 1. The ceramic and stainless steel plates were chosen to prevent the chemical oxidation and corrosion of the machine. Similarly, stainless steel equipment and air exhauster were used to avoid further corrosion. Potassium hydroxide (KOH) and potassium nitrate (KNO_3) were the chosen chemicals for polishing CVD diamond film and were heated to their boiling point. The rotation speed of the ceramic plate at 82 rpm was the same as that of the mechanical polishing, and the swing frequency of diamond film was 20 min^{-1}, also the same as the mechanical polishing method.

2.2.2. Thermo-chemical polishing

This study also experimented with thermo-chemical polishing, another method that can be used to obtain diamond films.

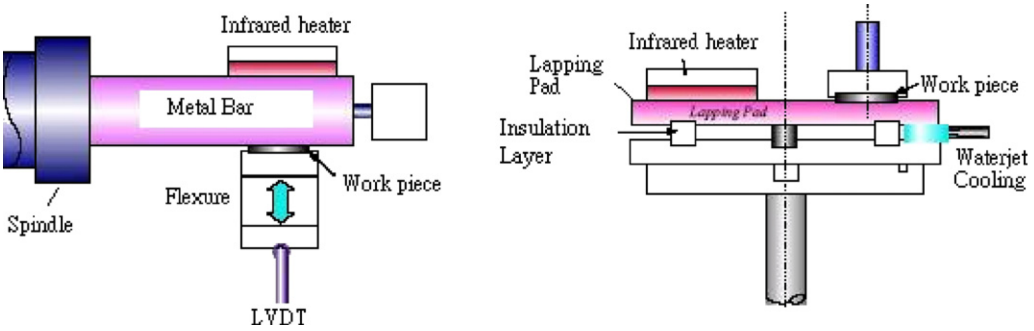


Fig. 2. Schematic diagram of the setup for thermo-chemical polishing experiments.

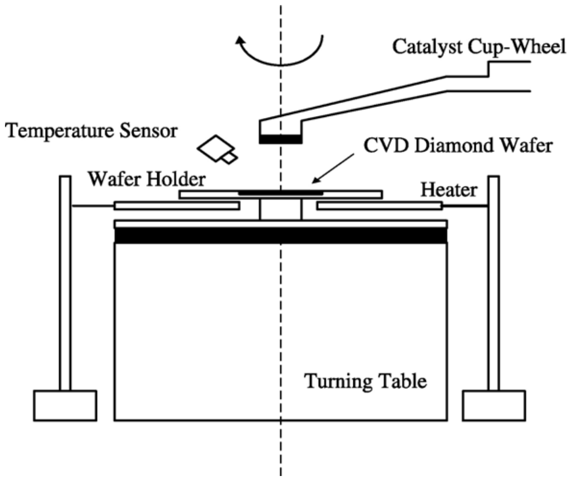


Fig. 3. Schematic diagram of experimental setup for diamond planarization.

Fig. 2 shows the schematic diagram of the setup for hot polishing experiments. The iron/steel bar or plate was heated by either infrared irradiation or inductive heating devices to various skin temperatures. In the case of turning experiments, the specimen was mounted on a flexure and was then brought to contact with the heated iron/steel bar. The contact force was monitored through the displacement of the flexure.

The relative speed and duration of polishing were also recorded. Some millimeters of the iron/steel bar or plate surface were taken off with a turning/dressing tool each time before starting the next new set of experiment to ensure that surface conditions remained the same.

2.2.3. Excimer laser ablation

This study used the excimer laser Lambda Physik LPX200 series (ArF 193 nm) which has a maximum repetition rate of 100 Hz, maximum pulse energy of 400 mJ and pulse duration of 20 ns. A MicroLas homogenizer and ×10 condenser lens were used to homogenize the beam and increase the fluence. The CVD diamond film, horizontally placed on an XY stage, was irradiated in air by the excimer laser at a 90° angle of incidence. The laser spot size was approximately 1.4 mm × 1.4 mm.

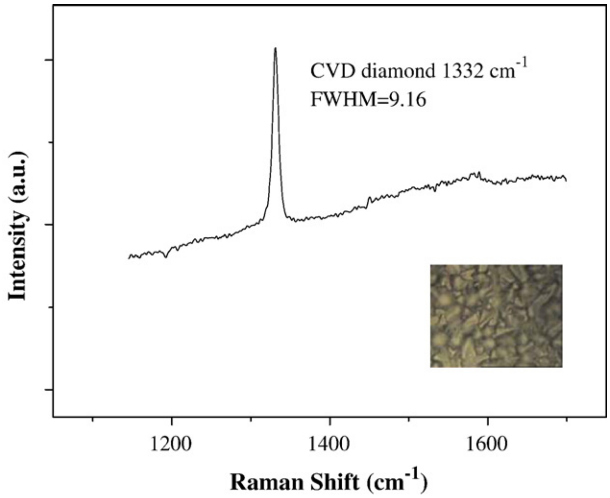


Fig. 4. Raman spectrum of as-grown CVD diamond film.

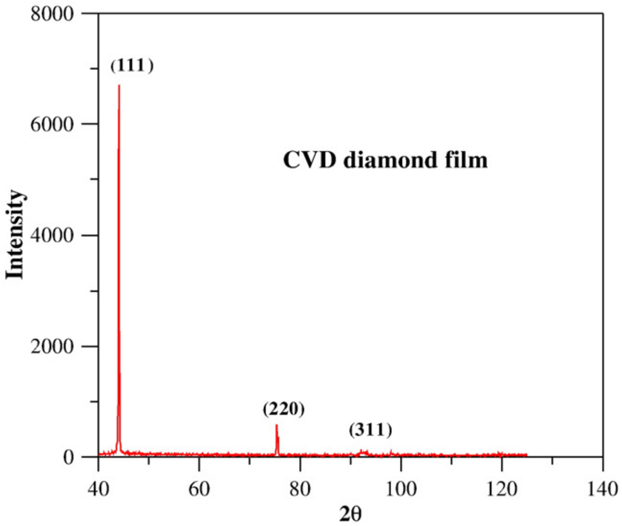


Fig. 5. XRD inspection of CVD diamond film samples.

2.2.4. Catalytic reaction assisted grinding

A catalytic grinding cup wheel was developed in order to shorten the machining time and decrease surface roughness of diamond film. Cast iron was used as the main catalyst and the binder in the primary catalytic grinding wheel. Furthermore, grits were made of diamond abrasives with TiC coating and the grit size was mesh 800. Therefore, the catalytic reaction occurred on the contact area between the grinding wheel and the diamond surface when grinding. Then the diamond surface structure was converted into a graphite structure with lower hardness than CVD diamond to make the polishing process easier. The catalytic reaction and grinding, which when combined together are called "dual processes," reduced the diamond surface roughness easily.

Fig. 3 illustrates a schematic diagram of the experimental setup to process CVD diamond film in the present study. The facility was modified from a back grinder machine and included a rotational vacuum chuck table, a rotational air spindle, a dumbbell wafer holder and a heating system. The diamond wafer was maintained in place on the wafer holder by the suction of the vacuum chuck table. The heating apparatus was designed to heat wafers without rotating them in order to increase reaction activity between the diamond surface and the catalytic grinding wheel.

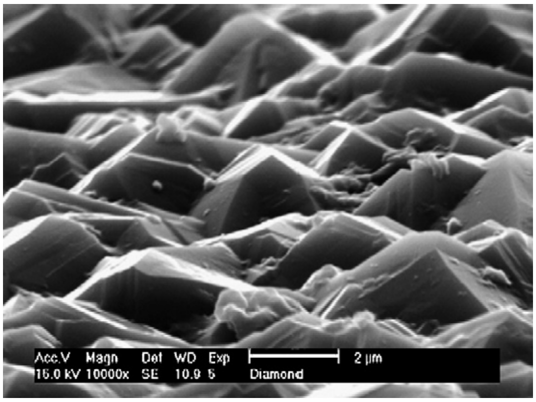


Fig. 6. Surface morphology of the CVD diamond films before polishing.

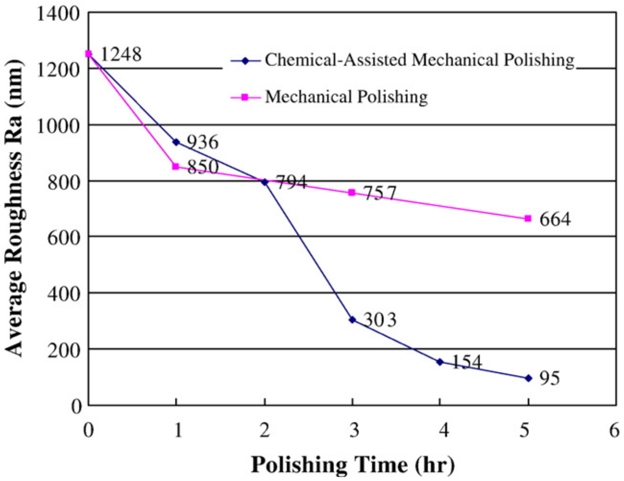


Fig. 7. Relationship between the average surface roughness of the diamond film and the polishing time with mechanical polishing method and chemical-assisted mechanical polishing method.

2.3. Characterizations

The polished diamond surfaces were observed with scanning electron microscope (SEM), Raman spectroscopy and atomic force microscopy (AFM). The analytical tools include: Philips SEM Model XL30 to observe the surface morphology before and after polishing, AFM of Digital Instruments Dimension 3100 scanning probe model to obtain the polished surface roughness, and Form Talysurf profiler to obtain the machined surface roughness by the cutoff length of 0.08 mm to 0.8 mm. The samples were measured on nine surface areas to obtain the average surface roughness after polishing.

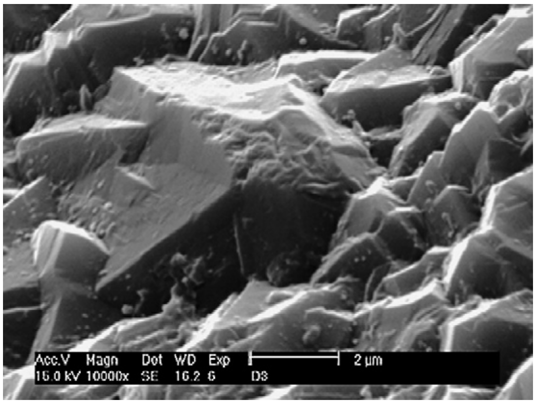


Fig. 9. Surface morphology of CVD diamond film polished by mechanical method.

3. Results and discussion

A 20 µm diamond film on 15 mm × 15 mm silicon substrate was prepared at 850 °C. In order to define the orientation of diamond crystals, as well as the quality, the surface morphology, and the

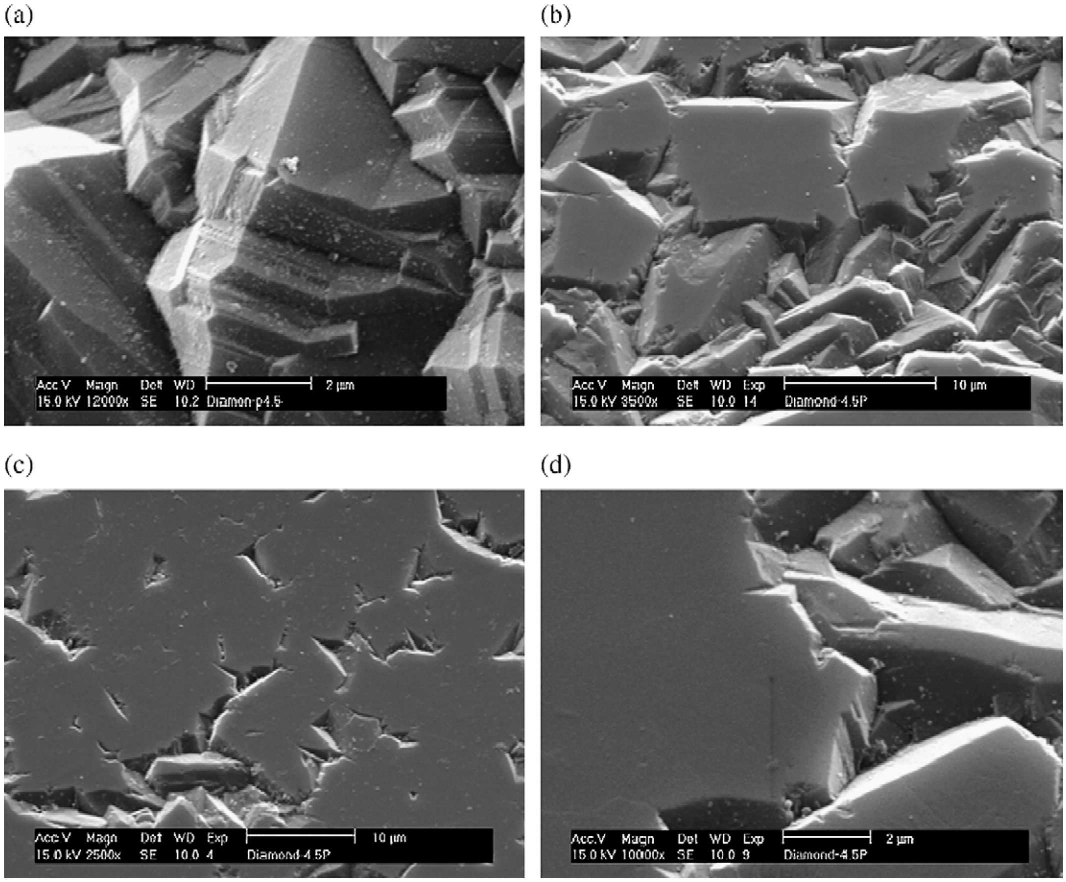
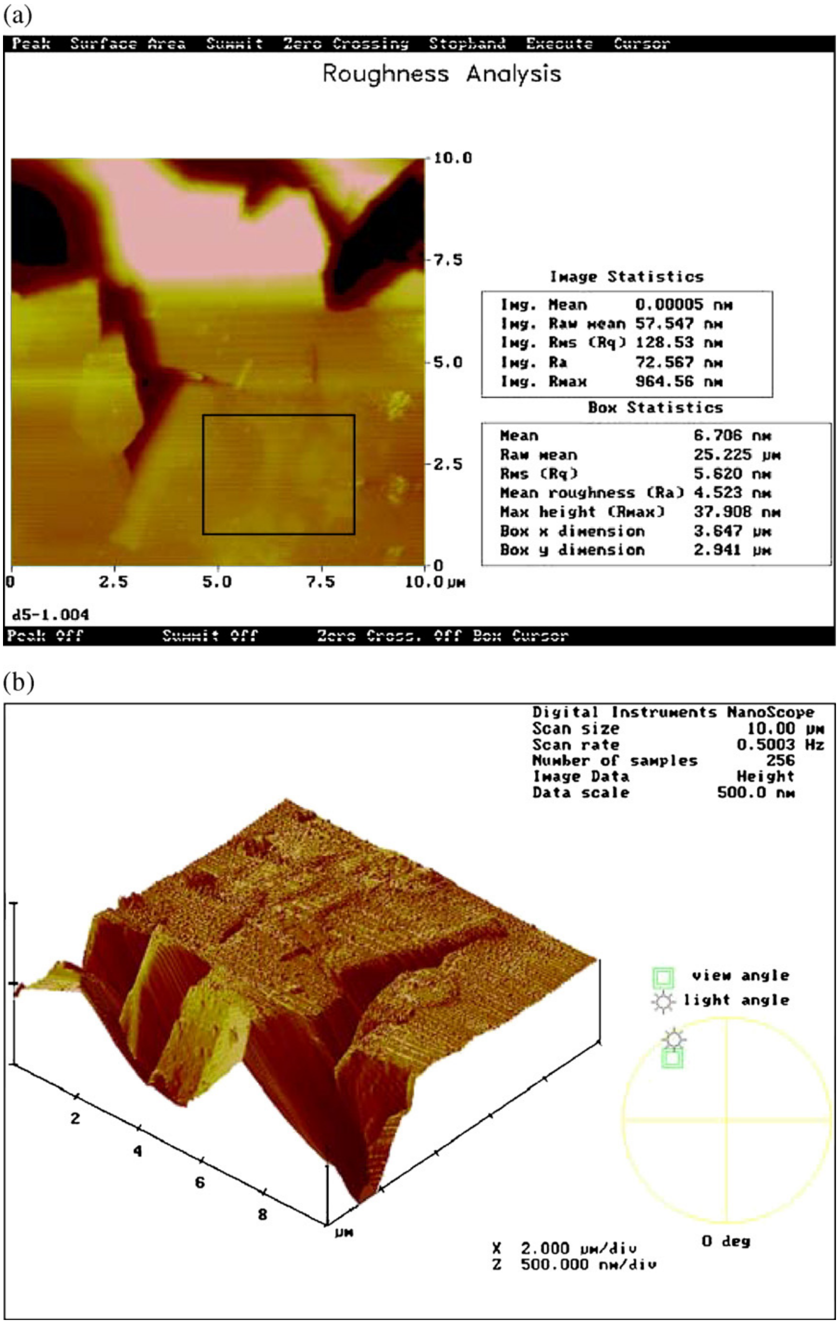


Fig. 8. (a) Surface morphology of sample polished after the first one hour by chemical-assisted mechanical polished method; (b) surface morphology of sample polished after three hours; (c) surface morphology of sample polished after five hours; and (d) there is almost no scratch on polished diamond crystals (enlarged from (c)).

surface roughness of the diamond film, the samples were totally characterized by SEM, Raman spectroscopy, AFM and X-ray detector before the beginning of the experiments. The Raman spectroscopy results showed that the diamond spectra peak was at 1332 cm^{-1}, while the peak of the graphite phase was not detected at 1550 cm^{-1}. The full width half magnitude (FWHM) was less than 10 wavenumbers at 1332 cm^{-1} Raman peak as shown in Fig. 4, which reveals a good hardness quality of CVD diamond. And Fig. 5 shows that the orientation of diamond crystals was almost (111) by X-ray. As for the surface morphology, the SEM image shown in Fig. 6 revealed that the surface roughness of the diamond film was very high before polishing.

3.1. Mechanical polishing and chemical-assisted mechanical polishing

The CVD diamond samples were polished for 5 h by the mechanical polishing method and the chemical-assisted mechanical method. The mechanical method was used in traditional polishing way with diamond powder, and the results were compared with the results of the chemical-assisted mechanical method. Although Brown's results show that the chemical-assisted mechanical method is a very effective way, the effect of chemicals must be controlled during polishing process [13]. The chemicals were heated up to their boiling



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Img. Raw mean 57.547 nm
Img. Rms (Rq) 128.53 nm
Img. Ra        72.567 nm
Img. Rmax      964.56 nm
Box Statistics
Mean                       6.706 nm
Raw mean                   25.225 μm
Rms (Rq)                   5.620 nm
Mean roughness (Ra) 4.523 nm
Max height (Rmax)   37.908 nm
Box x dimension            3.647 μm
Box y dimension            2.941 μm
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Digital Instruments NanoScope
Scan size              10.00 μm
Scan rate              0.5003 Hz
Number of samples         256
Image Data              Height
Data scale             500.0 nm
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X  2.000 μm/div
Z  500.000 nm/div
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Fig. 10. (a) AFM image of the sample after five-hour polishing by chemical-assisted mechanical polished method (Ra is 72.6 nm at the image of 10 μm × 10 μm; Ra is 4.5 nm at the boxed area); and (b) 3-D image of AFM results (the scan size is 10 μm).

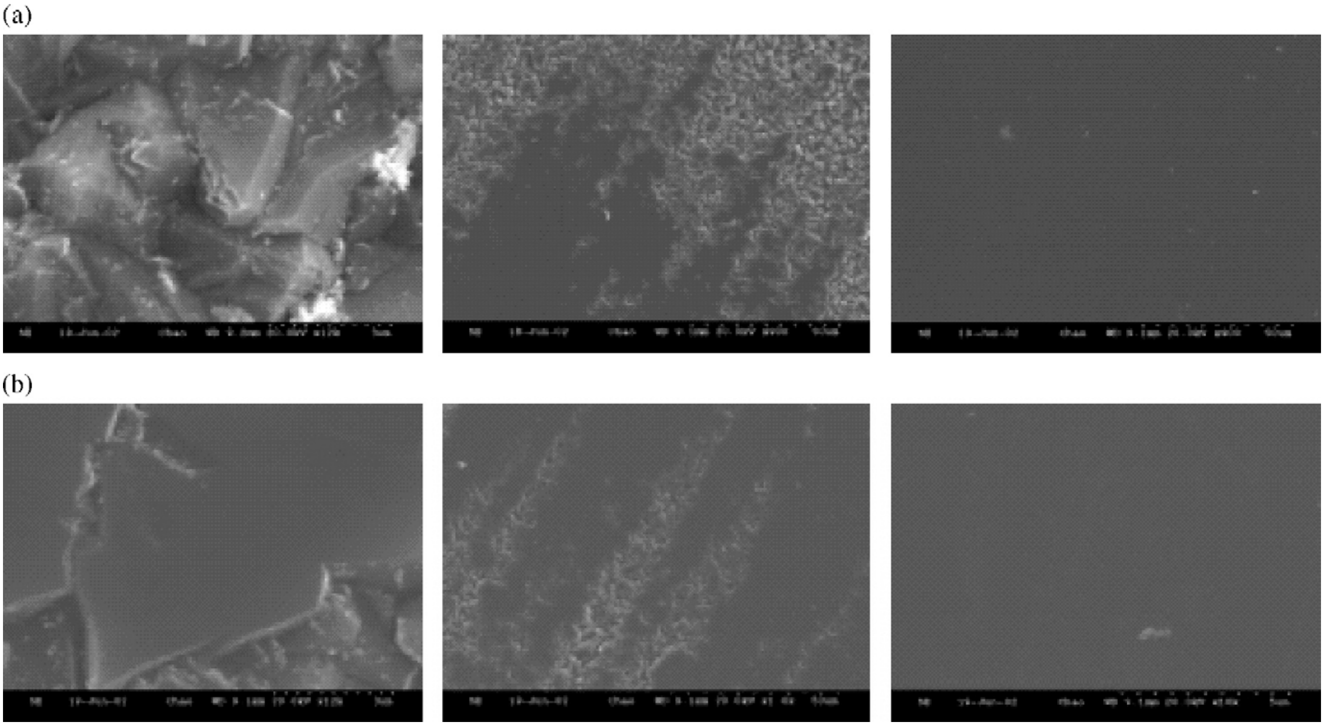


Fig. 11. (a) SEM micrographs of the thermo-chemical polished CVD diamond film after 10 min, 20 min, and 30 min with 5 μm scale bar (2.1 m/s, 450 °C, 3.8 MPa). (b) SEM micrographs of the thermo-chemical polished CVD diamond film after 10 min, 20 min, and 30 min with 5 μm scale bar (4.27 m/s, 30 min, 450 °C, 4.2 MPa).

point and then the diamond film was removed by the rotating ceramic plate. The results of surface roughness of the polished diamond film are shown in Fig. 7. The surface roughness obtained by chemical process decreased to a similar level as the result of the mechanical polishing method, which was about 800 nm, after the first two hours of polishing. After the third hour in the chemical-assisted mechanical process, the surface roughness was quickly reduced to 303 nm. Finally, in the fifth hour of the polishing process, the surface roughness of the diamond film slowly decreased to 95 nm.

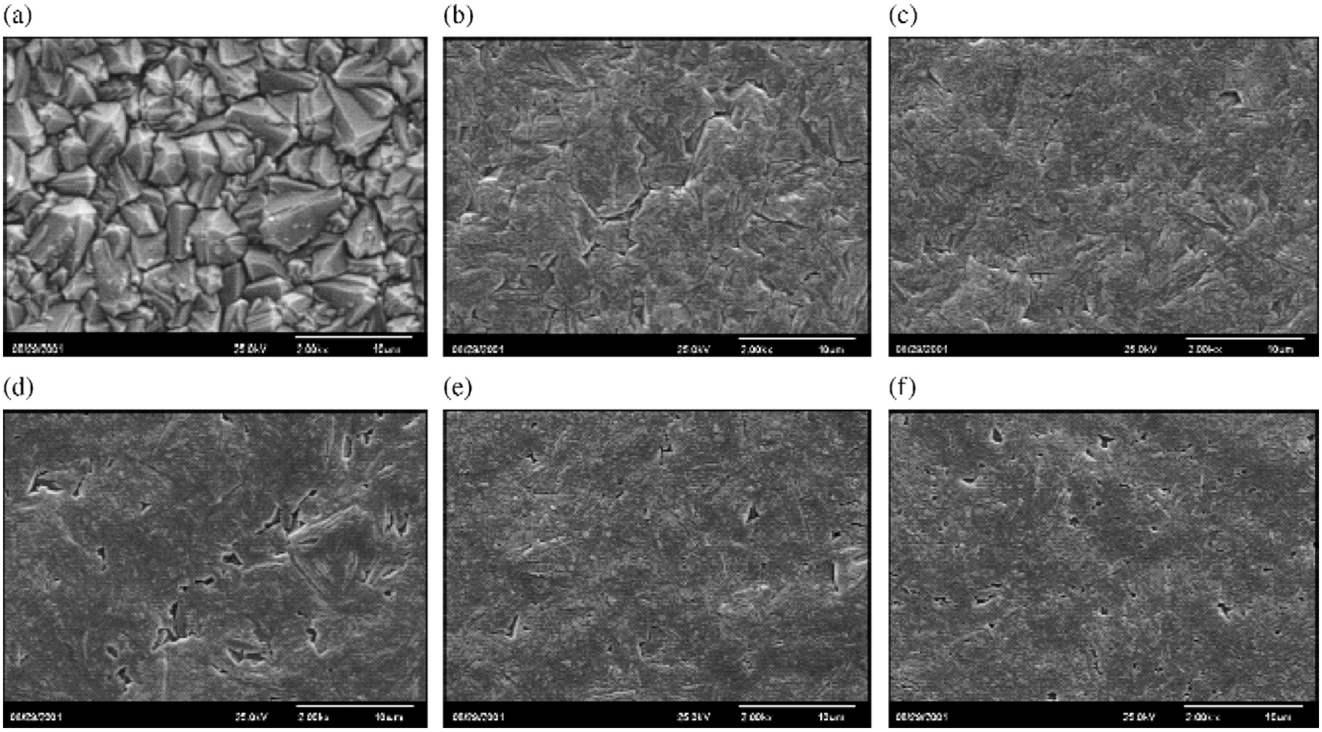
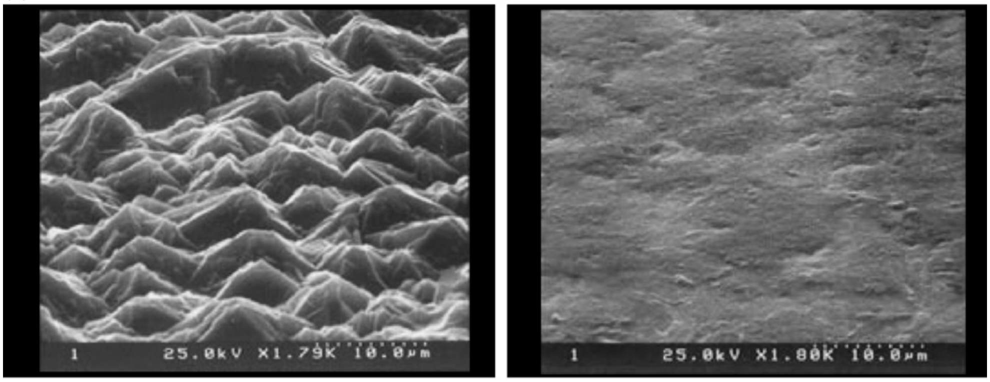


Fig. 12. Surface morphology of the (a) as-grown CVD diamond film, and after irradiation by excimer laser (193 nm, 385 mJ/10 Hz) for (b) 500 shots, (c) 1000 shots, (d) 3000 shots, (e) 5000 shots, and (f) 10,000 shots (the scale bars are 10 μm).

Experimental results raised the following questions: 1. Why did the roughness not decrease quickly at the beginning of the process? 2. Why were two stages/slopes observed during the 5-hour polishing process? The first question can be explained by the fact that the tips of pyramidal CVD diamond crystals were easily broken and removed at the beginning of the operation. Fig. 8(a) shows that the surface morphology of the samples was polished after the first hour of chemical-assisted mechanical polishing. The crystals almost kept their original rough shape except that some tips were removed and many nicks and grooves appeared on the surface of diamond crystals. The chemicals etched the tips and the weak grain boundaries of the diamond crystals, and hence some small crystals peeled off from the large crystals. The polishing time was not long enough to etch the whole diamond film in the first one or two hours, so the roughness decreased slowly. Furthermore, when the polishing time reached three hours, the surface roughness decreased quickly from 794 nm to 303 nm. As shown in Fig. 8(b), most of the tips of diamond crystals were broken or removed. From the results of the surface roughness and SEM images, the phenomena of two stages were explained. When the tips of the CVD diamond crystals were chipped and removed during the chemical-assisted mechanical polishing method, the surface roughness decreased quickly.

When the polishing time reached five hours, the surface roughness was down to 95 nm, and the surface morphology of some local areas looked very flat and smooth. From the SEM image shown in Fig. 8(c), almost all the pyramidal diamond crystals were machined to a plane surface, and there was no scratch on the plane of diamond crystals, as shown in Fig. 8(d). This kind of smooth surface without scratches was very different from the results obtained with mechanical polishing, as shown in Fig. 9. From Fig. 10(a) and (b), the AFM image shows the detail of the polished diamond crystals, and the average surface roughness Ra of the diamond crystal plane approaches 4.5 nm. If the surface roughness of the CVD diamond film could be obtained below 10 nm on the whole surface, the cost of the large polished area of the diamond film would substantially decrease. Fig. 10 provides even more information. The process for obtaining CVD diamond film

(a)



(left) before grinding

(right) after grinding

(b)

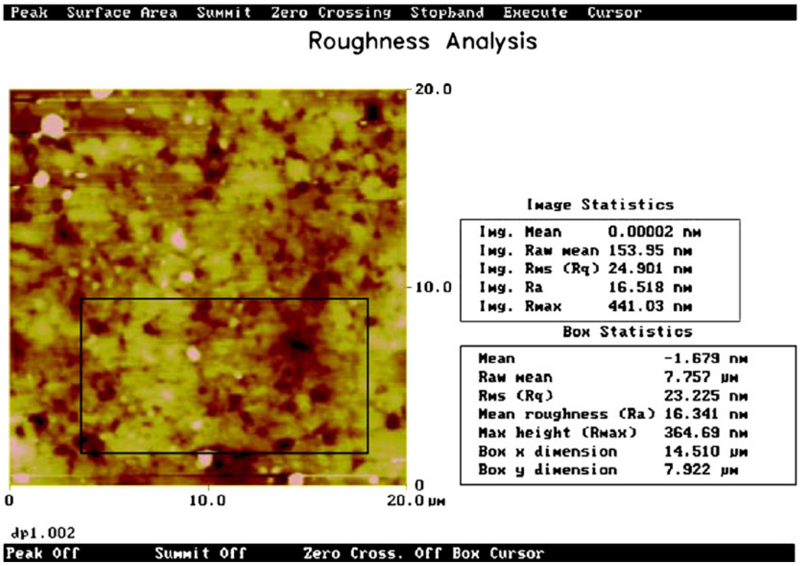


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           Image Statistics
Img. Mean      0.00002 nm
Img. Raw mean 153.95 nm
Img. Rms (Rq) 24.901 nm
Img. Ra       16.518 nm
Img. Rmax     441.03 nm
              Box Statistics
Mean                     -1.679 nm
Raw mean                  7.757 µm
Rms (Rq)                 23.225 nm
Mean roughness (Ra)      16.341 nm
Max height (Rmax)        364.69 nm
Box x dimension          14.510 µm
Box y dimension           7.922 µm
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Fig. 13. Diamond film surface morphology. (a) SEM image, left is before processing, (left) before grinding, right is after processing, (right) after grinding. (b) AFM image of ground diamond film.

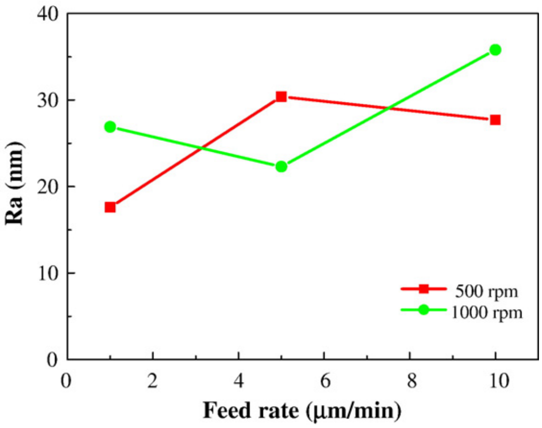

Fig. 14. Diamond film surface roughness in different feed rates.

consisted of transforming carbon into diamond, and hence, cavities and grain boundaries were also formed at the same time. If the diamond crystals are bigger, the cavities and the cracks between crystals will be larger and more numerous. This kind of natural structure was the obstacle to achieve the whole smooth plane with excellent surface roughness on angstrom scale. Generally speaking, the lower the surface roughness of the diamond film was, the smaller was the loss of the sound signal or the optical signal. This high quality of diamond film is perfect for use in electronic devices or some other applications.

3.2. Thermo-chemical polishing

The material removal mechanism involved in the thermo-chemical polishing process is generally categorized into graphitization, diffusion, oxidation and formation of metal–carbon complex. Cast iron and steel with various carbon contents were used in this study as the catalysts to transform diamond into graphite, which was subsequently removed by micro-chipping during the polishing process or diffusion into the iron/steel surface. The polishing temperature, pressure and speed used in the present study ranged from 50–650 °C, 0.5–4.5 MPa to 2.0–5.7 m/s, respectively. The iron/steel bar or plate was preheated to the polishing temperature before the polishing experiments were carried out and the temperature was monitored during the polishing process by both infrared detector and thermocouple. Owing to the heat generated by the friction, the temperature at the contact zone should be higher than the preheated temperature. Fig. 11(a) and (b) shows the SEM micrographs of the CVD diamond films which were hot polished for 30 min under different polishing speeds (2.1 m/s and 4.27 m/s) at an average temperature of 450 °C. Based on the obtained results, some 1.5 μm and 4.8 μm thickness of diamond film was successfully removed in 30 min in the case of polishing at a temperature around 450 °C and at 2.1 m/s and 5.7 m/s, respectively.

3.3. Excimer laser ablation

The micrograph of the surface of the as-grown CVD diamond film and the micrograph of the diamond surface irradiated by excimer laser (193 nm, 385 mJ/10 Hz) for 500, 1000, 3000, 5000, 10000 shots are shown in Fig. 12. The surface roughness (Ra) value was improved from 1.1 μm of the as-grown diamond film to Ra ~ 0.1 μm in 500 shots. The peaks of the diamond grains were removed mainly by the photothermal effects introduced by excimer laser. The high energy density and short pulse duration of excimer laser play an important role in raising the temperature of the protruding diamond grains to an evaporating point. However, as the protruding peaks are gradually removed from the surface, the polishing rate decreases.

3.4. Catalytic reaction assisted grinding

From the SEM images, as shown in Fig. 13, the surface morphology of the diamond film was changed during this process. After the processing, the original pyramidal structure on the surface was smoothed, and the average surface roughness (Ra) also decreased.

The feed rate and the spindle speed were the key parameters considered in the present study. The feed rate was chosen as 1 μm/min, 5 μm/min, and 10 μm/min, while the spindle speed was chosen as 500 rpm, 1000 rpm, and 2000 rpm. The total feed of the spindle was 10 μm for each run. After processing, the average surface roughness (Ra) was measured by AFM. Fig. 14 shows the experimental results. As evidenced in Fig. 14, the average surface roughness increased with the feed rate. The spindle speed has an unapparent influence on the change of the average surface roughness. Furthermore, better surface quality was obtained from the lowest feed rate and the lowest spindle speed by the present facility.

3.5. Discussion

Table 1 summarizes the results of different polishing methods. The catalytic reaction assisted grinding method produced a good surface roughness in a few minutes, while the thermo-chemical polishing method had a relatively high

Table 1
Comparison of different processing methods for CVD diamond film

Method\item	Researcher	Ra	Machining time	Large area	Cost
Mechanical polishing	Current study	664 nm	5 h	Good	Low
	[Yoshikawa]	800 nm	1 h		
Chemical-assisted mechanical polishing	Current study	95 nm (4.5 nm locally)	5 h	Good	Low
	[Zaitsev]	6 nm	–		
	[Ollison]	2.8 nm	5 h		
Thermo-chemical polishing	Current study	25 nm (~9 μm/h)	0.5 h	Fair	Medium
Excimer laser ablation	Current study	100 nm	Few minutes	Poor	High
	[Ozkan]	1000 nm	50 s		
Catalytic reaction assisted grinding	Current study	16 nm	Few minutes	Good	Medium
	[Yoshikawa]	1100 nm	1 h		

material removal rate. However, the possibility of large area application and the cost of the different processes should be taken into consideration for further industry purpose.

4. Conclusion

Several polishing methods have been applied on high quality CVD diamond films. The catalytic reaction assisted grinding method performed a good surface roughness (16 nm) in only a few minutes. This preliminary result reveals great potential for commercial application.

Acknowledgements

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