Chemical-Assisted Mechanical Polishing of Diamond Film on Wafer

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Keywords: diamond film, polishing, surface roughness, material removal rate.

Abstract. Diamond has been well recognized a strategic engineering material. It possesses excellent physical and chemical properties including the highest hardness and thermal conductivity, and good resistance to chemical erosion. Although CVD diamond film has good potential outstanding properties, its industrial applications have been limited by the non-uniform thickness and rough surface. In the current study, the CVD diamond film is polished by the chemical-assisted mechanical method with different slurries. These slurries contain strong oxidation chemical and diamond powder. During the process, the diamond film was held against the rotational ceramic plate with transverse oscillation at 90 \(^\circ\) or lower. The profilometer, atomic force microscope and scanning electron microscope were used to evaluate the surface integrity of the diamond films before and after polishing. Based on the experimental results, the slurry containing potassium persulfate (K\(_2\)S\(_2\)O\(_8\)) produces the highest material removal rate while potassium permanganate (KMnO\(_4\)) develops the best local surface roughness. The strategy of using potassium persulfate for coarse polishing followed by potassium permanganate for fine polishing yields the diamond films of the best global surface roughness. The average surface roughness of the diamond film produced by the proposed technique is below 10 nm after 5 hours.

Introduction

Diamond possesses some of the most extreme physical and chemical properties, including the highest hardness, the highest thermal conductivity, wide optical transparency, chemically very inert. Because of these excellent properties, they render it appropriate for numerous mechanical, optical, thermal, and electrical applications [1]. The synthetic diamond was made by chemical vapor deposition (CVD) method [2]. A wide variety of methods forming diamond have been developed and CVD diamond can be grown on a large substrate [3]. Although CVD diamond film has good potential outstanding properties, the columnar growth of CVD diamond results in a polycrystalline nature and the grain size increase with film thickness [4]. Its industrial applications have been limited by the non-uniform thickness and rough surface. To overcome these limitations, CVD diamond films need to be polished to meet the requirement. However, polishing of diamond is a very difficulty task since it is the hardest and the most chemically inert material known in the nature. Over the past years, several methods have been employed to polish diamond [5], such as the mechanical polishing, thermo-chemical polishing, chemical-assisted mechanical polishing and planarization (CAMPP), laser polishing, ion beam polishing, and reactive ion etching. Considering the cost and performance, the most promising method appropriate for polishing appears to be chemical assisted mechanical polishing using strong oxidizing agents as slurries to polish CVD diamond films.

Experimental setup

The polycrystalline diamond films were prepared by the microwave plasma chemical vapor deposition on silicon substrate. The growth parameters employed are shown in Table 1. The thickness of the diamond film was 20 \(\mu\)m, the arithmetic surface roughness (\(R_s\)) was from 200 to 300 \(\mu\)m, and the maximum peak-valley height roughness (\(R_t\)) was 4-8 \(\mu\)m under the depositing condition (Table 1).
Table 1: Conditions of preparation of CVD diamond film

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<table>
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<tr>
<td>Substrate material</td>
<td>Si</td>
</tr>
<tr>
<td>Substrate size (mm)</td>
<td>15×15×1</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>800</td>
</tr>
<tr>
<td>Atmosphere pressure (mbar)</td>
<td>130</td>
</tr>
<tr>
<td>CH₄ in H₂ (vol%)</td>
<td>6</td>
</tr>
<tr>
<td>Microwave power (KW)</td>
<td>60</td>
</tr>
</tbody>
</table>

In the current study, strong oxidizing agents were chosen based on the reduction potentials in the chemical reactions [6]. The reduction potential value can indicate how oxidative the chemical is. The higher the value is, the more oxidative the chemical is. The authors selected six oxidizing agents, including potassium nitrite (KNO₃), potassium chlorate (KClO₃), potassium dichromate (K₂Cr₂O₇), potassium permanganate (KMnO₄), hydrogen peroxide (H₂O₂), and potassium persulfate (K₂S₂O₈) to assist mechanical polishing. We prepared each reagent on saturated liquid state at room temperature and mixed with suitable amount of dilute sulfuric acid to make the reduction reaction occur (Table 2).

The experiment was divided into two parts. In the first part, the diamond films were polished with each oxidizing agent on the same polishing condition, load 4kg, temperature 70, and speed 200rpm. One can observe which reagent was suitable for polishing diamond films roughly. Based on the results of the first-part experiment, four proper reagents for the second-part experiment were chosen. In the second part, the factors were set the down force 1 and 4 kg, temperature 70 and 90, and rotational speed 100 and 200 rpm.

During the polishing process, CVD diamond film was held against a rotational ceramic plate with a transverse oscillation. The chamber was heated to a constant temperature and a load was applied to the sample when proceeding. A slurry containing oxidizing agent and diamond powder of size 4-8 μm used for increasing removal rate was dripped onto the groove ceramic plate and spread over the whole surface. After polishing procedure, we used the ultrasonic vibration to clean the contamination on the CVD diamond films in a 2:1 solution of H₂SO₄ and 30% H₂O₂ at 80.

A Raman spectroscopy was used to optically characterize the CVD diamond films. The average surface roughness were taken by a stylus profilometer with tip radius of curvature 2.5 μm at 9 points on samples. An atomic force microscope (AFM) was also employed to determine surface roughness on fine polished films. A scanning electron microscope (SEM) was used to investigate the morphology and orientation of the films. A linear variable displacement transducer (LVDT) device was used to measure the thickness of CVD diamond films before and after polishing and we acquired the material removal rate of diamond.

Results and discussion

Preliminary experiment The first experiment was used to investigate the effective reagent for polishing diamond films. Fig. 1 is a plot of the average surface roughness of the diamond films polished by different slurries versus the polishing time at the same polishing conditions of down force 4 kg, temperature 70, and rotational speed 200 rpm. The water with diamond powder as slurry to polish diamond film was also used for reference. As can be seen, the surface roughness decreases with polishing time. The most significant decrease in Rₐ occurs within the first hour of polishing, as the applied force is acting concentratedly on the tip of diamond crystallite. One can further observe that the slurries are separated into two groups, upper four and lower three curves. The lower three curves are the slurries containing potassium permanganate (KMnO₄), potassium persulfate (K₂S₂O₈), and hydrogen peroxide (H₂O₂) respectively. It is attributed to the fact that their reduction potentials are higher than others as seen in Table 2, which means the chemical action is triggered more actively.

Table 2: Standard reduction potentials at 1 M, 298 K, 1 atm [6]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>E⁰/V</th>
</tr>
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<tbody>
<tr>
<td>NO₂⁻ + 4H⁺ + 3e⁻ → NO + 2H₂O</td>
<td>0.957</td>
</tr>
<tr>
<td>ClO₂⁻ + 3H⁺ + 2e⁻ → HClO₂ + H₂O</td>
<td>1.214</td>
</tr>
<tr>
<td>Cr₂O₇²⁻ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O</td>
<td>1.232</td>
</tr>
<tr>
<td>MnO₄⁻ + 8H⁺ + 5e⁻ → Mn²⁺ + 4H₂O</td>
<td>1.507</td>
</tr>
<tr>
<td>H₂O₄ + 2H⁺ + 2e⁻ → 2H₂O</td>
<td>1.776</td>
</tr>
<tr>
<td>S₂O₃²⁻ + 2H⁺ + 2e⁻ → 2HSO₄⁻</td>
<td>2.123</td>
</tr>
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When polished by these three slurries, the surface roughness was decreased from about 250 nm to 31 nm, while other four slurries offer the surface roughness down to 45 nm at most. Fig. 1 also tells that when water is used as slurry, the surface polishing is the least effective among the slurries. It illustrates that the oxidation agents do play a major role in the polishing diamond films.

**Primary experiment** Based on the results of the preliminary experiment, the best four slurries were selected, namely hydrogen peroxide (H$_2$O$_2$), potassium persulfate (K$_2$S$_2$O$_8$), potassium permanganate (KMnO$_4$), and potassium chlorate (KClO$_3$), for the primary experiment investigating the effects of the major processing parameters. Fig. 2 shows the surface roughness of the diamond films polished by hydrogen peroxide against time. When the polishing parameters are set for the down load 4 kg, rotational speed 200 rpm, and temperature 90℃, the surface is polished most rapidly. In four hours, the average surface roughness can reach 31 nm. On the other hand, polishing by 1 kg, 100 rpm and 70℃ produced the slowest reduction in surface roughness, and could only achieve 74 nm in Ra. In this figure, one finds that the main polishing factors are down load, rotational speed, and temperature in order. It means that higher load would primarily govern the surface roughness of polished diamond films, followed by higher speed and higher temperature. As has been known, the chemical is used to enhance the removal rate and to assist mechanical polishing. Particularly, when the chemical force of oxidation is matched with the mechanical force of chipping, it can create the best effect in polishing the diamond films. Hence, in the case of polishing by hydrogen peroxide, the high reduction potential produces large chemical force and the large mechanical force must be used to match for the best surface quality.

Fig. 3 shows the surface roughness of the diamond films polished by potassium persulfate against time. The result is very similar to that of hydrogen peroxide. Polishing by high load, high temperature, and high speed produces the best surface roughness. Inversely, polished by low load, low temperature, and low speed causes the worst surface quality. The difference between Fig. 3 and Fig. 2 is that the temperature is the second main factor governing the surface roughness of diamond films. It is considered the potassium persulfate at high temperature (resulted from high rotational speed) produced higher chemical force than the mechanical force.

Fig. 4 shows the surface roughness of the diamond films polished by potassium permanganate against time. Although the main factors affecting surface quality also follow the order of load, temperature and speed, high rotational speed does not warrant for good surface roughness. On the contrary, it must work in association with appropriate load and temperature. When the chemical and mechanical force supports each other at equilibrium, it produces the best polishing performance. In the case of polishing at 4 kg, 90℃, 100 rpm, the average surface roughness can be reduced to 29 nm after four hours. The minimum Ra can be even less than 20 nm in local area. The explanation for the results is that the reduction potential of potassium permanganate is intermediate as shown in Table 2. The oxidizer is not strong enough to polish diamond films at high speed.

Fig. 5 shows the surface roughness of the diamond films polished by potassium chlorate against time. The result is similar to that polished by potassium permanganate, while higher load produces worse surface roughness instead. It is considered the reduction potential of potassium chlorate is the lowest among the selected four reagents in Table 2. When the diamond films are polished at the load of 4 kg, the mechanical force is too large compared to the chemical force. It also illustrates the appearance of fractures on CVD diamond surface at high load. Hence the lower load associated with high temperature and low speed produces the best surface quality, and the average surface roughness can reach 36 nm.

In comparison with the best results in use of different slurries as shown in Fig. 6, each slurry is subject to an optimal set of polishing conditions for the best surface quality. The experimental results
Fig. 1 Average surface roughness of diamond films polished by different slurries at 4 kg, 70 °C and 200 rpm.

Fig. 2 Average surface roughness of diamond films polished by hydrogen peroxide.

Fig. 3 Average surface roughness of diamond films polished by potassium persulfate.

Fig. 4 Average surface roughness of diamond films polished by potassium permanganate.

Fig. 5 Average surface roughness of diamond films polished by potassium chlorate.

Fig. 6 Comparison of surface roughness of diamond films polished by different slurries.

tell that high temperature is the common necessary condition for all slurries. It indicates that one can provide enough mechanical force by the polishing equipment (such as the generated polishing speed and load), while the chemical force at the polishing condition is lower. When polishing by the slurry of potassium permanganate at 4 kg, 90 °C, and 100 rpm, one obtains the best surface quality and the surface roughness can be reduced to 29 nm. One can also see that the surface roughness seems to keep a constant level, that the further decrease in the roughness at the applied condition is hard.

The removal rate of diamond film is proportional to the rotational speed of polishing plate and the applied load. The effect of larger load is to increase the true contact area between the diamond film and polishing plate. However, one also finds that the increase in load causes the increase of the number of micro-cracks. Fig. 7 shows the removal rate of each slurry at 4 kg, 90 °C, and 200 rpm. One observes potassium persulfate yields the maximum removal rate, followed by hydrogen peroxide, to
Fig. 7 Comparison of material removal rate with different slurries at 4 kg, 90 °C and 200 rpm potassium permanganate, and potassium chlorate in order. The removal rate of diamond is proportional the value of reduction potential, and it can achieve 0.53 up to 1.39 µm per hour.

**Optimum polishing conditions.** Based on the above experimental results, the slurry containing potassium persulfate (K₂S₂O₈) produces the highest material removal rate, and potassium permanganate (KMnO₄) develops the best local surface roughness. The best way to obtain a mirror-like surface in the minimum time is using potassium persulfate for coarse polishing followed by potassium permanganate for fine polishing. The coarse polishing conditions are 4 kg, 90 °C, 200 rpm and potassium persulfate containing diamond powder of 4-8 µm as slurry. The fine polishing conditions are 4 kg, 90 °C, 100 rpm and potassium permanganate containing diamond powder of 0-0.5 µm as slurry. The surface roughness of 5.3 nm is obtained using the proposed polishing method in 4 hours of coarse polishing and 1 hour of fine polishing. However, there can be small areas in the center of CVD diamond film not being polished completely. It can be attributed to the difference of coefficient of thermal expansion between diamond and silicon substrate causes the sample warping and the concave surface. Polycrystalline diamond films grown by microwave plasma CVD were polished by an oxidation-enhanced mechanical polishing. The current method achieves a good surface roughness in a few hours compared to a few days by the conventional mechanical polishing. The observed polishing rate and surface roughness can reach 1.39 µm/hr and 29 nm under the appropriate conditions.

Fig. 8 shows the SEM micrographs of the CVD diamond films at different stages during the polishing. For as-grown polycrystalline diamond film, it shows very rough surface and contains well-facet crystalline with the average grain size of approximately 8 µm. As polishing proceeds, the
surface morphology is clearly changed. The original pyramidal-like structure on the surface is smoothed. When the polished area get larger, the pits of grain boundaries decrease therefore the finer surface roughness. After fine polishing, the resulted surface appears to be smooth with little visible texture and pits or voids between the crystallites. These pits are due to the polycrystalline nature of CVD diamond and limit the achievable smoothness of the polishing. In the process, CVD diamond film comes into contact with diamond powders causing the micro cracking. Meanwhile, the oxidizing agents function as accelerating the growth of these micro cracks. Thus higher removal rate than conventional mechanical polishing is obtained. However, it is unavoidable that some scratches and fractures appear on the surface, because the polishing mechanism yet partially includes micro chipping and abrasion.

As shown in Fig. 9, CVD diamond films are characterized by Raman spectroscopy to ascertain the purity. For the unpolished diamond film, the full-width half magnitude (FWHM) is less than 10 wave numbers at 1332 cm\(^{-1}\) Raman peak, and only one weak trace of non-diamond inclusion was identified, which reveals good quality of the as-grown diamond. After polishing, the Raman spectrum of the CVD diamond film is similar to the unpolished one with lower FWHM value. It reveals that there is no chemical contamination on the polished diamond film. Thus, better quality of CVD diamond is gained in use of the present technique.

![Fig. 9 Raman spectrum of CVD diamond film](image)

**Conclusions**

The optimum polishing conditions for a mirror-like surface in the shortest time were determined experimentally. The strategy of using potassium persulfate for coarse polishing followed by using potassium permanganate for fine polishing yields the diamond films of the best global surface roughness in short time. The average surface roughness produced by the proposed technique is below 10 nm in 5 hours. The obtained results reveal a good potential for the industrial application.

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Progress on Advanced Manufacture for Micro/Nano Technology 2005
doi:10.4028/0-87849-990-3

Chemical-Assisted Mechanical Polishing of Diamond Film on Wafer
doi:10.4028/0-87849-990-3.1225