Diamond Deposition at Low Substrate Temperatures in a Thermal Plasma Reactor

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Abstract

Diamond films have been successfully deposited on various substrate materials such as molybdenum, copper, and aluminum at low substrate temperatures ranging from 400 °C to 600 °C by thermal plasma chemical vapor deposition (TPCVD). Growth rates of diamond films higher than 40 μm/hour have been achieved using ethanol and methanol as precursors. Substrate surface pretreatments and a three-step deposition process have been explored to improve the adhesive properties of diamond films. Indentation test results showed that our diamond films deposited at low substrate temperatures had load versus lateral crack diameter slopes (dP/dx values range between 50 - 120 [kgf/mm]) comparable to high substrate temperature deposited films. The three-step process has been shown to yield the highest dP/dx values making it promising for future applications of diamond films in industry.

1. Introduction

Currently there are several key problems with chemical vapor deposition (CVD) of diamond films at low substrate temperatures (< 600 °C) which can be separated into three categories: growth rates, film quality and adhesion [1-4]. Growth rates have been found to be low, decreasing as the substrate temperature is lowered. Film quality, which can be defined by the film surface morphology, amorphous carbon content and crystallinity of the diamonds, has also been lacking. This is in part due to amorphous carbon content increasing and crystallinity degrading as the surface temperature is decreased. The final key problem with low temperature CVD of diamond films has been adhesion. While problems with adhesion plague conventional CVD processes [5], these problems are particularly pronounced in low temperature CVD.

Low substrate temperature CVD is required for numerous industrial applications because the high substrate temperatures (800-1200°C) required for conventional CVD processes exceed the melting point or result in undesirable phase changes in many materials such as aluminum, copper and tool steels. The primary objective of this research has been to develop a method for low temperature growth of diamonds (LTGD) in a thermal plasma reactor and to solve the problems associated with the process. We have attempted diamond deposition on various substrate materials at temperatures below 600°C. Multiple deposition processes, substrate pretreatments and operational parameter were investigated in order find the best conditions for LTGD.

2. Experimental Apparatus and Procedure

A schematic of the counter-flow liquid injection plasma reactor (CFLIPR) used in our research is shown in Fig. 1. The thermal plasma CVD system consists of a DC plasma torch, a water-cooled quartz tube reactor and quenching chamber with exhaust port, a substrate holder with central column liquid injection probe and a set of three MKS mass flow controllers. A more detailed description of the experimental set-up is given elsewhere [6]

Substrate temperatures have been monitored by a set of three K-type thermocouples inserted in the substrate 1 mm below the surface. Temperature calibration experiments were conducted to determine a correction factor for various materials, which allowed us to extrapolate the actual surface temperatures from the measured temperatures. All substrate temperature values have been corrected.

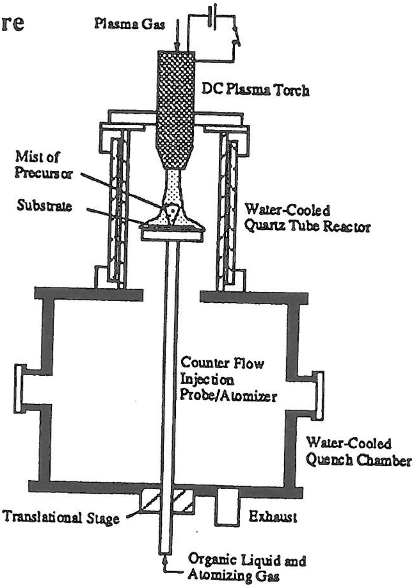

Fig.1. Schematic of the CFLIPR

The following precursors have been tested: ethanol, methanol, chlorinated hydrocarbons and methane. By injecting the precursor directly into the plasma jet we want to achieve full evaporation and dissociation of the precursor into hydrocarbons and atomic hydrogen which is necessary to form the diamond growth species on the substrate surface.

3. Results and Discussion

3.1. Pretreatment

Early in our experiments we recognized that diamond nucleation on the substrate surface at low substrate temperatures was facilitated by the use of pretreatments, as other researchers have reported [7,8]. While we found these pretreatment unnecessary for high temperature CVD processes, they were found to be absolutely necessary for LTGD.

Surface roughening in particular aided the growth of diamonds by providing nucleation sites. Surface roughening was achieved by sanding, polishing and sandblasting the substrate surface. The best results were achieved by sanding the substrate surface. Subsequent seeding of the substrate surface also aided LTGD. Variously sized diamond particles were used. We also attempted to mechanically imbed the diamond seeds on the surface by compression and to seed the surface by direct application of diamond seeds. The latter, combined with sanding the substrate surface, provided us with the best results.

3.2. Single-Step Deposition Process

We investigated various deposition processes in order to find a coating process which would result in high quality diamonds and good adhesion with high growth rates. We focused on two processes in particular based on their potential to meet our demands:

a one step and a three-step deposition process. Coating at low substrate temperatures by either process produced high quality diamond films at relatively high growth rates. SEM studies showed the deposited diamonds were well faceted and the surface morphology comparable to that of films generated in conventional CVD processes. Growth rates over 40 µm/hr were achieved, higher than reported elsewhere at reduced substrate temperatures [9]. The remaining problem is the poor film to substrate adhesion.

The single-step deposition (SSD) process produces a uniform, continuous film of diamond. An SEM micrograph of such a film on a Mo substrate grown at a substrate surface temperature of 560°C for a deposition time of 15 minutes can be seen in Fig. 2. The film consists of diamonds of fairly uniform crystal size, the diameter being slightly lower than 10 µm. The substrate was initially polished, followed by surface roughening, ultrasonic cleaning and diamond seeding. As shown in Fig. 2 (sample SSD1) the quality of the diamond film is comparable to that produced at high substrate temperatures.

An experiment at high substrate temperatures was performed (Sample SSD2) in order to allow us a comparison between high and low substrate temperature film characteristics. Identical conditions, with the exception of diamond seeding, were used. A substrate temperature of 1030°C for a net deposition time of 25 minutes was used.

Indentation tests were performed to evaluate the adhesion of the deposited film to the substrate on both samples using an Instron 8511 Tensile Testing Machine with a standard Rockwell C Diamond Tip, Brale Indentor. Predetermined loads were applied to the sample followed by recording the lateral crack lengths on an SEM. Fig. 3 shows a plot of the load versus lateral crack diameter for samples SSD1 and SSD2. Based on a study performed by Jindal *et al* [10] the better the adhesion of the film to the substrate the lower the crack diameter for a given load. Therefore the higher the slope of the graph of load versus lateral crack diameter (dP/dx), the better the adhesion.

It is important to note that the lateral crack diameter was determined by drawing a circle around the tips of the farthest reaching cracks emanating from the indentation site. and then using the resulting area to find an equivalent radius. Other researchers have not specified how they acquired the lateral crack length in their results [10,11,12] which makes a direct comparison of dP/dx results impossible. However since our measurements are based on the longest crack lengths, we can be certain that our results are conservative and hence a rough comparison is possible.

A load which does not result in cracking of the film is below the critical load. If a crack does appear at a given load then this load is above the critical load. Since it is very difficult to find the exact load at which cracks first appear we have given our critical load results in the form of a range, based on the load right before and after which cracking is first observed, as other researchers have done [11,12]. Our test results for SSD films show that the slope (dP/dx) of the load versus lateral crack diameter and critical load of the high and low temperature deposition processes are nearly equivalent (See Table 1).

An X-ray diffraction pattern was taken of sample SSD1 and the diffraction lines associated with diamond and graphite were observed. Since we did not have Raman spectroscopy available for this sample, the identification of the diamond phase was only performed by observation of the crystal structure.

3.3. Three-Step Deposition Process

A patented three-step deposition (TSD) process [13] was also investigated to see whether film to substrate adhesion could be improved. The single-step deposition process is preferable because of its simplicity. However, if adhesion in the TSD process is superior to the single-step deposition process then the former would be preferred.

The first step in this process involves nucleation of diamond crystals by thermal plasma CVD, with substrate temperatures not exceeding 600 °C. The objective of the first step is to create a <u>non</u>continuous, well distributed sprinkling of diamond crystals, as shown in Fig. 4.

The second step involves electroplating a filler material onto the substrate to fill the spaces between crystals and to anchor them to the substrate surface. Possible electroplating materials include copper, nickel, molybdenum or alloys. Fig. 5 shows an angled view of the substrate surface after the second step. It is evident that the filler material, copper in this case, coats the bottom of the crystals, immersing them partially and providing the desired anchoring effect.

After a brief heat treatment the third step in the TSD process involves the "re"deposition of diamond at a substrate temperature of approximately 500°C. Fig 6 shows a top view of a sample having undergone the third step. As can be seen the film and crystal size (5 to 8 μm in diameter) is fairly uniform. The diamond quality also seems to be satisfactory based on visual inspection. Again an X-ray diffraction study provided verification of the presence of carbon, molybdenum and copper as surface elements.

A cross-sectional view of the substrate after the TSD process revealed no amorphous carbon. Also, the cross-boundary growth of crystals seemed to provide strong intercrystal adhesion. In order to locate the position of diamond, copper and molybdenum on the cross-section a WDS (Wavelength Dispersive Spectroscopy) mapping was performed. Carbon made up the top layer and could be seen to penetrate the middle layer composed of copper. Traces of copper in the molybdenum substrate were also evident resulting from Cu to Mo diffusion during the heating of the substrate.

Indentation tests, used to evaluate the adhesion of the films, indicated that the critical load was not constant across a given film-substrate interface. Rather the adhesion, and hence the critical load to initiate crack propagation, varied from position to position by 15 - 20%. Some areas evidenced better adhesion and diamond growth than others. This is believed to be a result of the counterflow injection. Diamond deposition is optimized in certain areas of the substrate based on atomic hydrogen and carbon presence. Deposition in a counterflow liquid injection reactor does not result in a uniform species distribution in front of the substrate as would be desired to maximize uniformity of film adhesion .

Fig. 7 shows a plot of the applied load versus lateral crack diameter for samples TSD2, 3 and 4. The critical load and the dP/dx values for the given samples are presented in Table 1. It is evident that the TSD process yields better results in terms of adhesion than the single-step deposition process. It is also evident that the TSD films have equivalent adhesion dP/dx values as found by other researchers [11,12] performing high temperature deposition studies.

4. Summary and Conclusion

Substrate pretreatment experiments showed that roughening of the surface with subsequent diamond seeding improved the nucleation of diamond crystals and adhesion of the film to the substrate. Deposition experiments were conducted at substrate temperatures below 600°C producing crystalline diamond films at growth rates over 40 µm/hr on molybdenum, copper and aluminum. Film adhesion using the TSD process is equivalent to the adhesion results of other researchers conducting CVD at substrate temperature of 880 to 980 °C [11,12].

It is important to note that the experiments performed by other researchers involved substrate materials such as tungsten, tungsten carbide and SiAlON whereas our indentations tests were conducted on molybdenum only. The indentation test gives imperfect results for films of thickness < 50 µm because the hardness of the substrate material will affect the critical load and slope of load-crack length results. Therefore discrepancies exists if film indentation tests are compared when the substrate materials differ. This problem has been documented and analyzed by other researchers [10].

Our indentation tests were conducted on the same substrate materials in areas where the film based on visual and SEM inspection was uniform. By testing similar areas of the film we also avoided dealing with the problem of varied film thickness. Finally, our indentation tests were performed at least 5 mm from the edges of the film so as to avoid edge effects. Indentation tests have shown the low substrate temperature TSD films to be comparable in adhesion to high substrate temperature deposited films.

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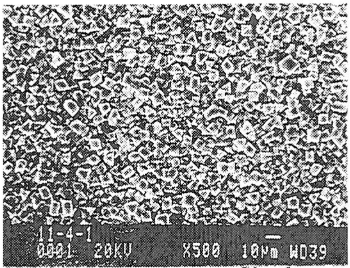

Fig. 2. Continuous Single Step Deposition Film

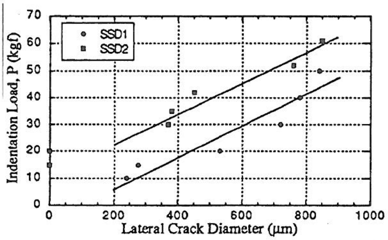

Fig. 3. Single Step Deposition Indentation Test Results

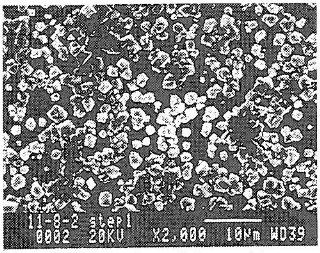

Fig. 4. First Step Three Step Deposition, Particle Distribution

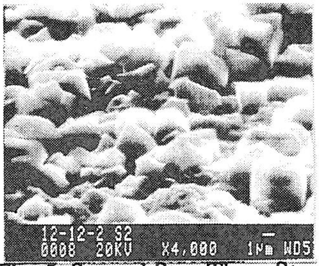

Fig. 5. Second Step Three Step Deposition, Electroplated Film

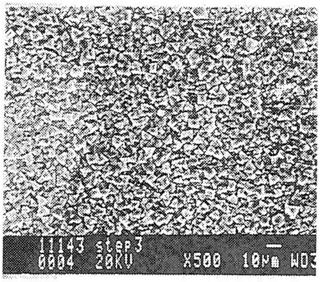

Fig. 6. Third Step Three Step Deposition, Continuous Film

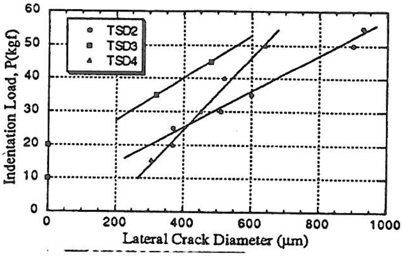

Fig. 7. Three Step Deposition Indentation Test Results

Table 1. Comparison of Different Indentation Test Results

Sample #	Critical Load (kgf)	dP/dx (kgf / mm)	T_{sub} (°C)	Ref.
SSD1	<10	56	560	
SSD2	between 20 - 30	52.5	1030	
TSD2	≤ 20	50.6	535	
TSD3	between 20 - 30	75	540	
TSD4	between 10 - 20	113.2	525	
W2	< 10	133	980	[12,13]
WC3	between 10 - 20	118	880	[12,13]
SiAlON1	between 20 - 30	60	880	[12,13]

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