ORIGINAL ARTICLE

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Experimental investigation of the parameter dependency of the removal rate of thermochemically polished CVD diamond films

Abstract Parameters controlling the removal rate of chemical vapor deposition (CVD) diamond films thermochemically polished on transition metals in a mixed argon-hydrogen atmosphere were investigated. The ambient temperature, the pressure exerted on the diamond film, the angular velocity of the polishing plate, the frequency and the amplitude of the transverse vibrations were among the parameters used in the experiments. Temperature measurements showed that the removal rate was increased exponentially with increasing magnitude of the parameter. An exponential increase in the removal rate was also observed with increasing pressure and hence with increasing contact between the diamond film and the polishing plate. However, an exponential decrease in the removal rate was observed with increasing angular velocity of the polishing plate. The removal rate obtained with the application of transverse vibrations was more than three times that obtained without transverse vibrations. Moreover, the removal rate was seen to be higher at resonant frequencies. An increase in the removal rate with increasing amplitude of the transverse vibrations was also observed. Raman measurements carried out on the films to determine the presence of the non-diamond carbon layer after thermochemical polishing revealed non-diamond Raman lines only for films polished at 1000 °C and 1050 °C for the temperature range 750–1050 °C.

Key words CVD diamond film · Non-diamond carbon · Raman spectroscopy · Removal rate · Thermochemical polishing

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Introduction

Diamond films produced by chemical vapor deposition (CVD) have found a lot of useful applications in a variety of fields including the manufacture of electronic devices such as optical windows, field effect transistors, particle detectors, pressure sensors, etc. [1–6]. The possibility of making such devices is enhanced by effective polishing, which tremendously scales down the surface roughness of the diamond films. It is believed that smooth polishing reduces heat leakage and facilitates firm contacts with the diamond film. Over the years, several polishing techniques have been developed to scale down the surface roughness of CVD diamond films [7–11]. Although these techniques have in their various ways reduced the surface roughness of CVD film to levels suitable for electronic applications, they are not without limitations. The random orientation of the crystallites constituting the films renders techniques such as mechanical polishing incapable of reducing the surface roughness evenly in all planes and directions of the films [11]. Additionally, metal pieces which fall onto the surface of the film during mechanical polishing can cause scratches, thereby increasing the surface roughness of the polished surfaces.

The method of thermochemical polishing of CVD diamond films employed in this work overcomes the limitations imposed by conventional methods such as mechanical polishing. The thermochemical polishing method polishes diamond films successfully in all crystallographic planes and directions and achieves an ultrafine polishing quality on the nanometer scale in a time span of a few hours. The application of only small weights on the films ensures that the surfaces of the films are not distorted during polishing. The mechanism of thermochemical polishing has been discussed previously [10, 12–14]. Essentially, it involves the interaction of diamond with transition metals such as iron and nickel at high temperature and the consequent conversion of diamond into non-diamond carbon. The

non-diamond carbon subsequently diffuses into the metal. Hydrogen has been characterized as the most suitable ambient atmosphere for accelerated thermochemical polishing of CVD diamond films. The choice of hydrogen lies in its catalytic capability to interact with carbon and eventually remove it from the polished surface [10, 15].

The objective of this work is to investigate the parameter dependency of the removal rate of diamond films during thermochemical polishing. The parameters investigated were the ambient temperature, the pressure exerted by the small masses, the angular velocity of the polishing plate, the frequency of the transverse vibrations and the amplitude of the transverse vibrations. The knowledge of the relationship between the removal rate and these parameters provides information about the condition under which rapid polishing can be attained.

Experimental

A schematic cross-section of the thermochemical polishing apparatus used in the polishing of the CVD diamond films is shown in Fig. 1. The diamond film is sandwiched between the polishing plate and the weight. The polishing plate is driven by a step motor which receives rectangular positive pulses from a drive board through the frequency generator. An additional drive board ensures either a continuous one-directional rotation covering 200 steps per revolution on the one hand, or a two-step forward, one-step backwards motion on the other hand, depending on which of the two switches is selected. The velocity of the polishing plate can be regulated by selecting the desired frequency from the frequency generator. For a continuous one-directional rotation, the velocity of the polishing plate is determined from the relation:

$$v_f = \frac{2\pi r f}{200} \tag{1}$$

where r is the radius of the polishing plate, f the frequency from the generator and the factor 200 is the number of steps in one complete revolution of the polishing plate.

An additional step motor is included in the configuration, the sole aim of which is to produce transverse vibrations that tear the polishing plate from the sample, thus reducing the frictional force between the two. The transverse vibrations also ensure that the upper weight and the sample do not rotate during the polishing process. This effectuates the simultaneous polishing of both sides of the sample. The vibrational step motor is programmed to produce to-fro half-step vibrations, two half-step vibrations, three half-step vibrations and four half-step vibrations as required. In this way, the amplitude of the vibrations can be selected at will. The frequency generator for this motor can operate between 100–1800 Hz. The amplitude A_i of the ith half-step vibrations is determined from the relation:

$$A_i = \frac{\pi r X_i^\circ}{180} \tag{2}$$

where r is the distance between the axes of the step motor and the polishing plate (more precisely, r is the length of the tungsten wire delivering the vibrations) and X_i° is the angle corresponding to the ith half-step vibration.

Although pure hydrogen is considered as the most suitable ambient atmosphere for this polishing method, the ambient atmosphere used in the experiments is a gas mixture comprising 4% hydrogen and 96% argon for safety reasons. This gas mixture replaces the air in the polishing chamber so that the diamond films do not oxidize at extremely high polishing temperatures (about 1000 °C). Previous work [10, 15] showed that the conversion of diamond (sp^3) into non-diamond carbon (sp^2) is slow in comparison to the dissolution of sp^2 carbon in the polishing plate for polishing temperatures

Fig. 1 Schematic representation of the experimental set-up of the thermochemical polishing apparatus

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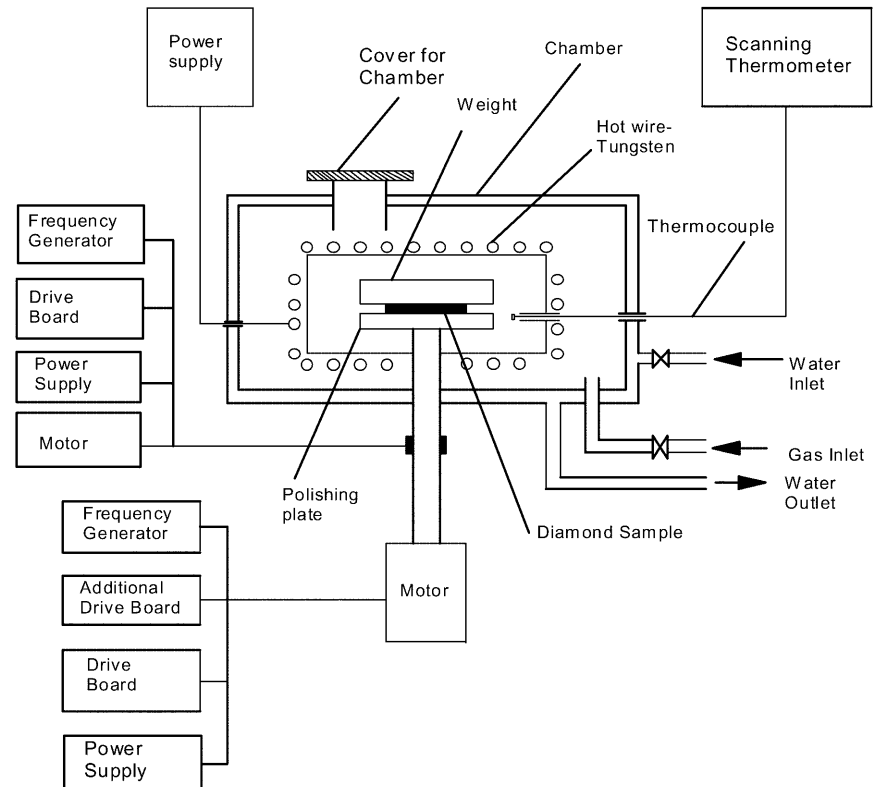
below 950 °C. However, at temperatures above 950 °C, the conversion of sp^3 into sp^2 carbon supersedes the dissolution of sp^2 carbon in the polishing plate. This is manifested by the presence of non-diamond carbon bands in the Raman spectra of the polished films. Steel of low carbon content is used as both the polishing plate and the weight placed on the diamond film to ensure contact between the film and the polishing plate. The spiral tungsten wire surrounding the polishing plate is heated electrically and the temperature in the chamber is measured by a scanning thermometer via a thermocouple. The gas pressure in the chamber is raised slightly above atmospheric pressure so that air from outside does not enter during polishing. The outer chamber is continuously cooled with water to keep it in thermal equilibrium with the outside surroundings.

The dependency of the removal rate on the above-mentioned parameters was investigated by polishing a quantity of CVD diamond films at selected values of each parameter. The thickness of the films was measured before and after polishing using a micrometer screw gauge. The removal rate was then obtained from the relation:

$$r_{exp} = \frac{R_0 - R}{t} \tag{3}$$

where R_0 is the thickness of the as-grown film, R the thickness of the film after polishing and t the time taken to polish the film.

An as-grown diamond film was polished at each selected value of a given parameter. All other parameters were kept constant during the investigation of the given parameter. Temperature measurement was done in the range 750–1050 °C in steps of 50 °C on different films. Pressure measurement was performed by applying small masses ranging between 2–12 g successively on different diamond films. The angular velocity measurement was done by increasing the frequency of the generator between 92–192 Hz in steps of 20 Hz. The measurement with transverse vibrations was done by increasing the frequency of the vibrational step motor in steps of 100 Hz between 0–700 Hz inclusively. The transverse amplitude was doubled, tripled and quadrupled and the measurement done on four different as-grown diamond films. A different polishing plate was used for each measurement. This was to ensure that the polishing plate did not become saturated with carbon atoms during polishing.

The optical micrographs showing the morphologies of as-grown and polished films, the results of the stylus profilometer measurement of the average surface roughness of the as-grown films and the atomic force micrographs (AFM) of the average surface roughness of the polished films have been presented in our previous work [16].

The optical grade CVD diamond films used in this work were processed by high-temperature plasma-enhanced CVD at the Fraunhofer Institute of Applied Solid State Physics in Freiburg, Germany.

Results and discussion

Temperature

Polishing was done in the temperature range 750–1050 °C in steps of 50 °C on seven different as-grown diamond films. Each film was polished for 8 h. During polishing, all the other parameters were kept constant at the following values: mass 11.704 g; rotation frequency 112 Hz; transverse frequency 450 Hz; transverse amplitude 3.46 mm. Raman measurements were done on the polished films to determine non-diamond carbon phases. Except for the films polished at 1000 °C and 1050 °C, the films polished at lower temperatures were free of
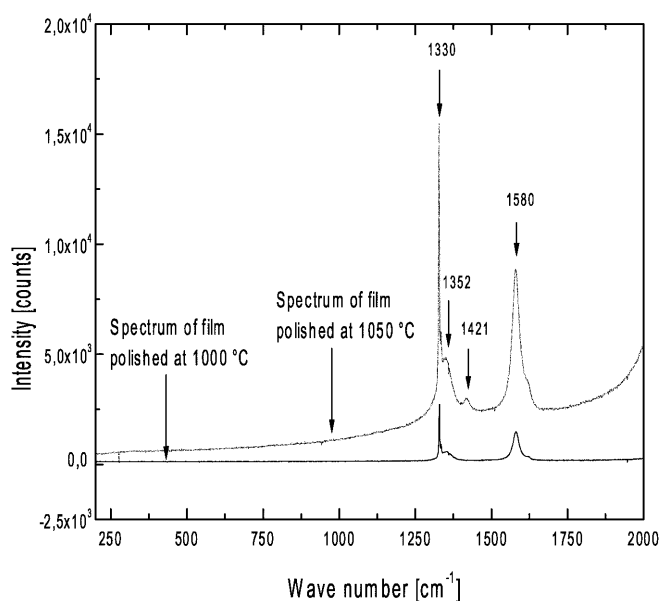

Fig. 2 Raman spectra of the films polished at 1000 °C and 1050 °C. The Raman diamond, the amorphous carbon and the graphite Raman lines can be seen on the same spectra. The non-diamond carbon layer is assumed to be less than 2 μm, which is about the penetration depth of the argon ion laser since the diamond Raman line appears in the spectra

non-diamond carbon. Figure 2 shows that the diamond Raman line and non-diamond carbon phases appear on the Raman spectra of the films polished at 1000 °C and 1050 °C. Since the depth of the argon laser used in the characterization was less than 2 μm, it is assumed that the layer made by the non-diamond carbon is correspondingly less than 2 μm thick. This is confirmed by the appearance of the diamond Raman line in the spectra.

Figure 3 shows the fitted curve of the experimental results. The curve shows an exponential increase in the removal rate with increasing temperature. The deviation of the experimental results from the fitted curve is within 12% error estimate. An Arrhenius plot of the temperature dependence is given in Fig. 4. Two distinct activation energies were determined from the plot. An activation energy of 0.52 eV was found for the temperature range 750–900 °C and an activation energy of 1.42 eV for the temperature range 900–1050 °C.

Pressure

The pressure dependency of the removal rate was investigated by placing light masses ranging between 2–12 g successively on eight different as-grown diamond films. Each film was polished for 8 h while keeping all the other parameters constant at these values: temperature 950 °C; rotation frequency 112 Hz; transverse frequency 450 Hz; transverse amplitude 3.46 mm. The polished films were characterized by the Raman method. Non-diamond carbon lines were absent in the Raman spectra of the films, manifesting that the removed
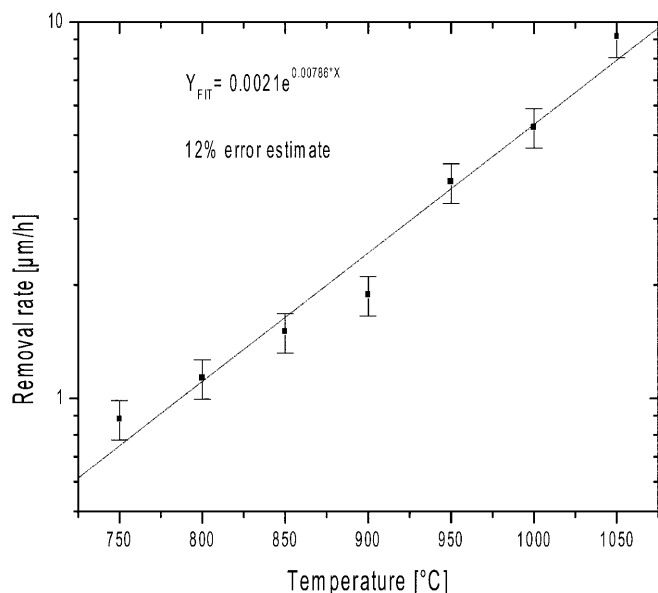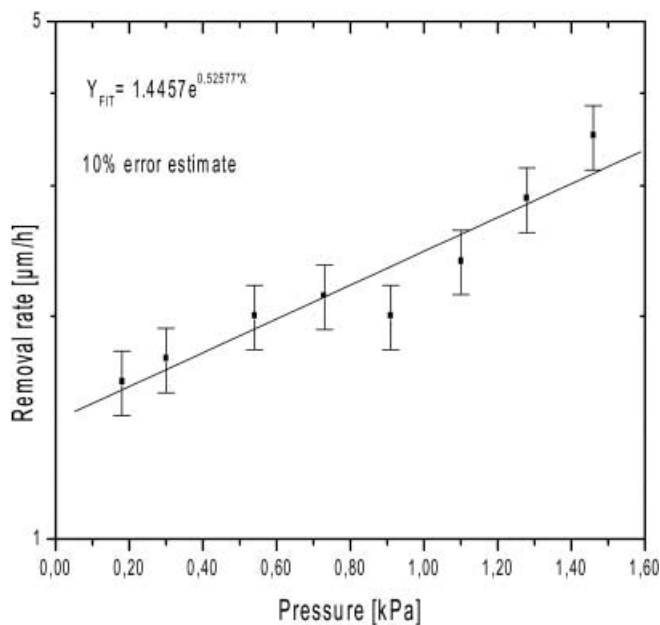
Fig. 3 Temperature dependency of the removal rate of seven diamond films thermochemically polished between 750–1050 °C in steps of 50 °C. The experimental results and the fitted curve agree within 12% error. The fitted curve shows that the removal rate increases exponentially with increasing temperature
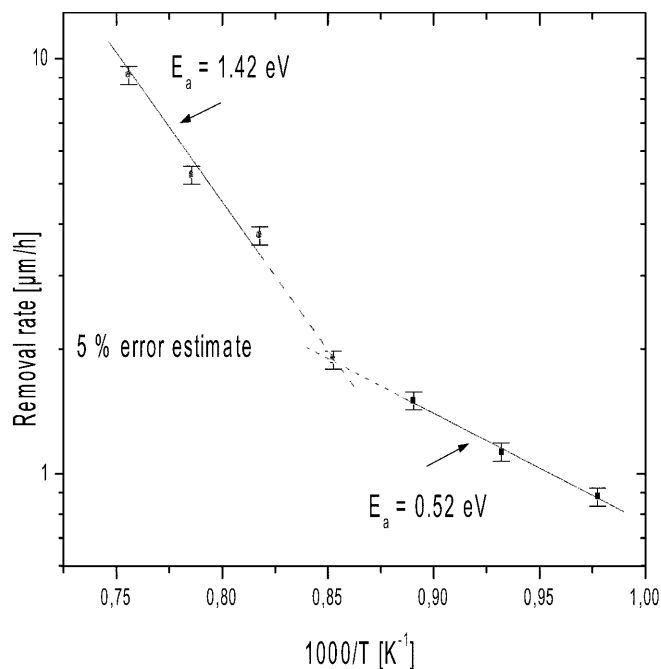
Fig. 4 Arrhenius plot of the temperature dependence of the removal rate of thermochemically polished diamond films. A thermal activation energy of 0.905 eV was determined from the curve

Fig. 5 Removal rate as a function of mass (pressure) exerted successively on eight diamond films during thermochemical polishing. The experimental and fitted curve correspond within 10% error estimate. The fitted curve shows an exponentially increasing relationship between the removal rate and the applied pressure

diamond dissolved completely into the polishing plate. The fitted curve for the experimental results is given in Fig. 5. The curve shows that the removal rate increased exponentially with increasing pressure exerted on the diamond film. It is believed that the pressure imposed on the films increases the contact between the surfaces of the polishing plate and the diamond film. The deviation of the experimental results from the fitted curve falls within 10%.

Angular velocity

The angular velocity of the polishing plate was altered by varying the frequency of the generator that delivers rectangular pulses to the step motor responsible for rotating the polishing plate. The frequency was increased in steps of 20 Hz between 92–192 Hz. The velocity of the polishing plate was determined from Eq. 1.

Six different as-grown films were used for the investigation. Each of the films was polished for 8 h. During polishing, all the other parameters were kept constant at these values: temperature 950 °C; mass 11,704 g; transverse frequency 450 Hz; transverse amplitude 3.46 mm. Again, the films were optically characterized by Raman spectroscopy. The spectra showed no detectable non-diamond carbon phases. As a result, the rate of dissolution of carbon into the polishing plate was clearly higher than the conversion rate of diamond into non-diamond carbon. The fitted curve of the experimental results is shown in Fig. 6. It is seen from the curve that the removal rate decreases exponentially with increasing angular velocity of the polishing plate. This effect can be related to the reduction of the surface contact between the diamond film and the polishing plate with increasing angular velocity. The deviation of the experimental results from the fitted curve falls within 5% error estimate.
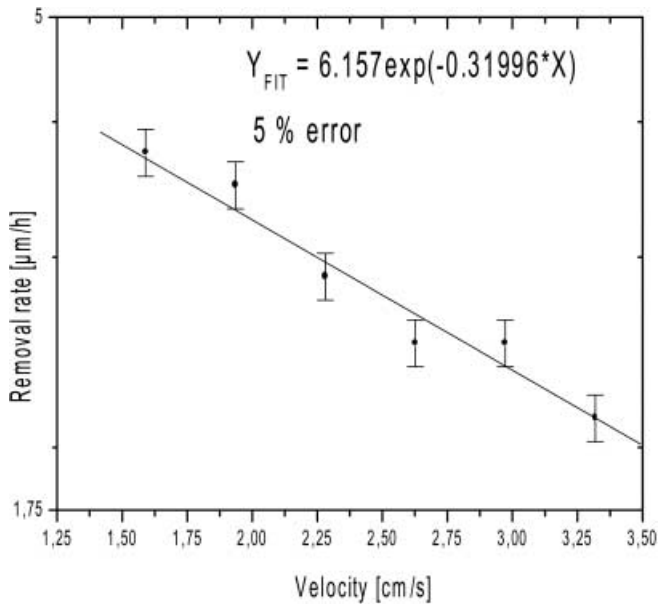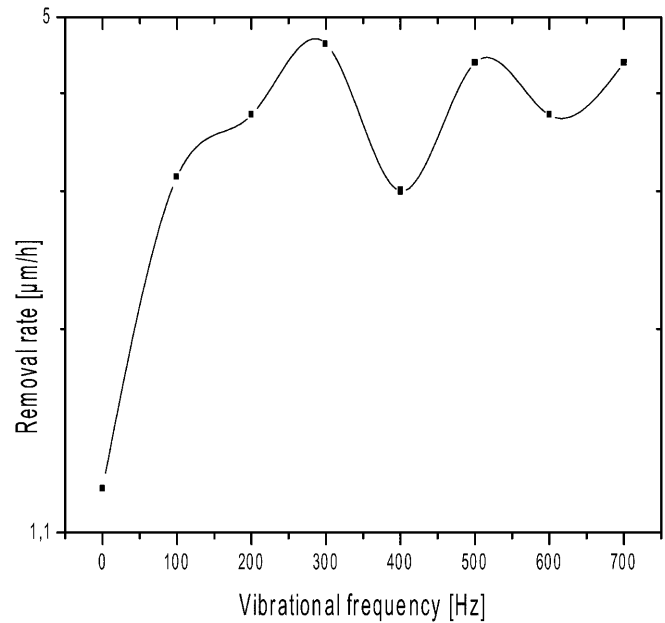
Fig. 6 The fitting curve shows that the removal rate falls exponentially with increasing rotational frequency (angular velocity). The deviation of the experimental results from the this curve falls within 5% error estimate

Fig. 7 The dependency of the removal rate on the transverse vibrations of the second step motor. The lowest removal rate is observed when no transverse vibrations are applied. The removal rate is seen to be high at resonant frequencies of the transverse vibrations

Transverse frequency

The transverse vibrations introduced into the measurement were produced by a second step motor. The vibrations were meant to tear the sample from the polishing plate so that the two did not adhere and consequently rotate with the same speed during polishing. The effect of these vibrations on the removal rate was investigated by varying the transverse frequency between 0–700 Hz in intervals of 100 Hz on eight different as-grown diamond films. Each of the films was polished for 8 h while the other parameters were kept constant as follows: temperature 950 °C; mass 11,704 g; rotational frequency 112 Hz; transverse amplitude 3.46 mm. Raman spectra of the polished films showed no non-diamond carbon lines, signifying a complete dissolution of the carbon atoms into the polishing plate. The experimental data are contained in the curve of Fig. 7. It is seen that the lowest removal rate was attained when no transverse vibrations were applied. The removal rate showed an irregular trend between 100–700 Hz. At 300, 500 and 700 Hz, the vibrations produced very loud sounds and the removal rate was observed to be higher at these frequencies than at all other frequencies. The frequencies at which these loud sounds were heard are believed to be the resonant frequencies.

Transverse amplitude

The amplitude of the transverse vibrations was increased by increasing the number of step vibrations between 0.5–

2.0 inclusively in steps of 0.5. Since there are 200 step vibrations in a complete revolution, a half-step vibration corresponds to an angle of 0.9°.

Thus, 0.9°, 1.8°, 2.7°, and 3.6° are the angles corresponding to 0.5, 1.0, 1.5, and 2.0 step vibrations, respectively. The amplitudes of the vibrations are then calculated from Eq. 2.

The investigation was performed successively on four as-grown diamond films. As in the previous cases, the other parameters were kept constant at the following values during the polishing: temperature 950 °C; mass 11,704 g; rotational frequency 112 Hz; vibrational frequency 450 Hz. The polished films were optically characterized and no traces of non-diamond carbon were seen in the Raman spectra. The experimental data were fitted by the curve shown in Fig. 8. From the curve, an exponential increase in the removal rate was observed with increasing amplitude. The deviation of the experimental data from the fitted curve fell within 2%. It is believed that high amplitudes are necessary to tear the diamond film from the polishing plate during thermochemical polishing so that the film does not adhere to the plate and hence rotate with a common speed.

Conclusion

The conversion of diamond into non-diamond carbon and the subsequent dissolution of the carbon atoms into the transition metal used as the polishing plate is enhanced by the selection of appropriate magnitudes of
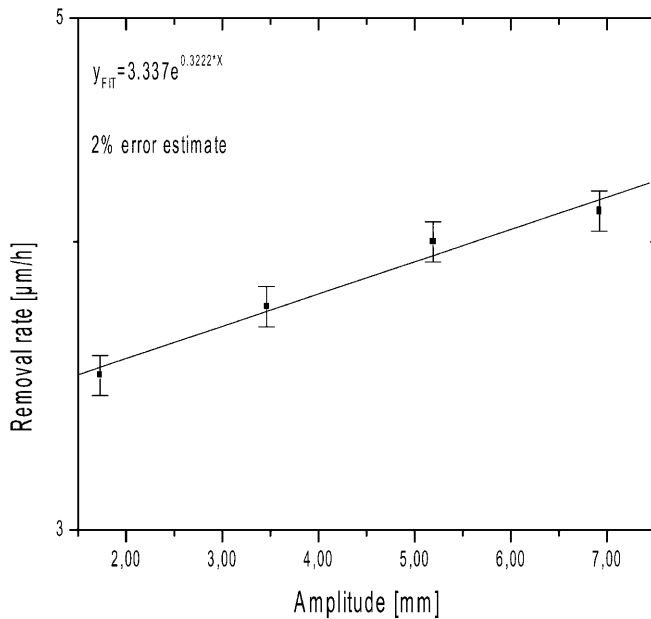
Fig. 8 Removal rate as a function of the amplitude of the transverse vibrations. The non-linear fitted curve shows an exponential increase in the removal rate with increasing amplitude. The deviation of the experimental results from this curve falls within 5% error estimate

the polishing parameters. It is seen that the ambient temperature, the pressure exerted on the diamond film and the amplitude of the transverse vibrations all increase the removal rate exponentially with increasing magnitudes of the parameters. Both the conversion and diffusion rates are temperature dependent. It was observed that when polishing was done at temperatures below 950 °C, all the converted diamond diffused into the polishing plate. It was only at temperatures above 950 °C that non-diamond carbon lines were seen in the Raman spectra of the diamond films. It is believed that the diffusion rate dominates at temperatures less than or about 950 °C and the conversion rate dominates at temperatures above 950 °C. The increase in the removal rate with increasing pressure applied on the film is due to the pressure-enhanced surface contact between the polishing plate and the film. By increasing the amplitude of the transverse vibrations, the adhesive force between the diamond film and the polishing plate is drastically reduced. Polishing without transverse vibrations has revealed the lowest removal rate. This is because, in the absence of transverse vibrations, the film and the polishing plate adhere and rotate together during polishing. Thus, polishing is considerably hampered. In essence, transverse vibrations are necessary during thermochemical polishing in order to tear off the diamond film from the polishing plate. In this way, the polishing plate and the film do not adhere and, consequently, the diamond film does not rotate alongside the polishing plate. Polishing at the resonant frequency or at the overtones of the resonant frequency of the transverse vibrations produces higher removal rates than at other frequencies.

This could be due to the fact that at resonant frequencies the adhesive force between the film and the polishing plate is reduced to the minimum. The removal rate is seen to drop exponentially with increasing speed of the polishing plate. This drop is attributed to the reduction in the surface contact between the diamond film and the polishing plate. In essence, an accelerated removal rate is reached when thermochemical polishing is done at elevated temperatures, when there is very good contact between the sample and the polishing plate (through high pressure applied on the diamond film and low angular velocity of the polishing plate), and when the adhesive force between the polishing plate and the film is minimum (through polishing at the resonant frequency and high amplitude of the transverse vibrations). It is worth noting that a high removal rate does not imply good quality polishing. However, since previous work has shown that smooth polishing is attained at low temperatures (750 °C), we believe that final smooth polishing can be attained at such low temperatures when there is good contact but no adhesive forces between the diamond film and the polishing plate.

The theory of thermochemical polishing is rather complex and cannot be determined without tedious mathematical calculations, leading to considerable assumptions and hence error. However, we are presently working on the theoretical determination of the conversion and diffusion rates and diffusion constants for diamond films polished with this method. The results will be presented in our next contribution.

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