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THE EFFECT OF GAS FLOW RATE ON DEPOSITION RATE USING CVD

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ABSTRACT

Solid thin films have been deposited on stainless steel 314 substrates in a hot filament thermal chemical vapor deposition (CVD) reactor at different flow rates of natural gas. The variation of thin film deposition rate with the variation of gas flow rate has been investigated experimentally. During experiment, the effect of gap between activation heater and substrate on the deposition rate has also been observed. Results show that deposition rate on SS 314 increases with the increase of gas flow rate. It is also seen that deposition rate increases with the decrease of gap between activation heater and substrate within the observed range. In addition, friction coefficient and wear rate of SS 314 sliding against SS 304 under different normal loads are also investigated before and after deposition. The obtained results reveal that the values of friction coefficient and wear rate are lower after deposition than that of before deposition.

Keywords: Deposition rate, Gas flow rate, CVD.

1. INTRODUCTION

Chemical vapor deposition (CVD) is a process in which a solid material formed from a vapor phase by chemical reaction, is deposited on a heated substrate. The controlling parameters in CVD process are surface kinetics, mass transport in the vapor, thermodynamics of the system, chemistry of the reaction and processing parameters like temperature, pressure etc. The deposition rate which is the prime limiting factor in a CVD process is mainly controlled by the formation of required species to be deposited and its transportation in the vapor and surface kinetics [1-3]. Thin film synthesis via chemical vapor deposition (CVD) has been the subject of active research over the last two decades. Numerous studies have been carried out to examine the effects of the process parameters, such as temperature of the substrate and filament, gas flow rate, gas composition, chamber pressure etc on different types of materials [4-9]. The CVD process of thin film growth may be divided into two important sequential steps, the transport of the radicals through the gas toward the surface and their consumption on the surface leading to the crystal growth. Experimental results and numerical calculations of thermal conduction and diffusion have shown that the mass transport in the gas phase plays an important role during thin film growth, and growth of thin films are mainly controlled by the mass transport rate rather than by the surface reaction rate at substrate temperatures [10, 11]. Gas flow rate is an important parameter for CVD thin film growth because the gas flow rate is closely related to the gas transport in the CVD reactor [10]. To date, efforts have been made to investigate the effects of the gas flow rate on thin film growth and conflicting results have been reported by different groups. Celii et al. [12, 13] reported that varying the gas flow rate could change markedly the resultant microcrystalline diamond (MCD) crystal texture and surface morphology but has little effect on the growth rate. Yu et al. [14] have found that CVD thin film growth by hot filament CVD depends on a mass transfer controlled process and the growth rate was increased by increasing the gas flow rate, while other groups have reported that the gas flow rate does not appear to have a significant influence on thin film growth [15, 16].

From the previous experimental study discussed above it can be concluded that several experiments were conducted at different gas flow rate conditions and the effects on thin film growth differ significantly. Even now a day, the effects of gas flow rate on thin film deposition for different materials, especially, at varying gap between substrate and activation heater is less understood. This means that more work is needed for a better understanding of CVD film deposition under different gas flow rate, gap and other related parameters. Therefore, in this study an attempt is made to investigate the effect of gas flow rate and gap between activation

heater and substrate on the thin film deposition rate on SS 314. With its remarkable physical properties, thin film coatings on different substrates are expected to have many applications in industrial and engineering fields. A low friction coefficient combined with a very low wear rate is two of the numerous advantages which make it suitable for machining.

However, the tribological behavior of thin film deposition on SS 314 is yet to be clearly investigated. Therefore in this study, experiments are also conducted to observe the tribological properties of SS 314 under deposited and undeposited conditions.

It is expected that the application of these results will contribute to the different concerned mechanical processes.

2. EXPERIMENTAL DETAILS

2.1 Hot Filament CVD Unit

A thermo-chemical vapor deposition (hot filament) setup (Fig.1) was designed and fabricated. The set-up is a CVD system comprised a reactor chamber supported by some sub assemblies and sub systems. The sub assemblies are (i) Heater (ii) Connector and (iii) Cooling line; and the subsystems are (i) Gas evacuation system (ii) Electric supply system (iii) Heating system (iv) Cooling system (v) Gas supplying system (vi) Measuring system and (vii) Structure and handling system. These arrangements of the experimental setup (Fig.1) are similar to the conventional thermo-chemical vapor deposition (hot filament) unit. The substrate as shown in Fig.1 is placed on the substrate holder in between substrate heater and activation heater.

To deposit carbon, thermal CVD requires high temperature, generally from 800 to 2000^{0}C, which can be generated by resistance heating, high frequency induction, radiant heating, hot plate heating, or any combination of heating systems. Resistance heating is used here to obtain the required temperature. In substrate heating, there is a rectangular opening at the top of the substrate heater box. The substrate is placed through the opening, so that heat generated from Nichrome heater, inside the rectangular box is transferred through the opening to the substrate as required by adjusting the supply voltage to the heater by variac. Activation heater operates directly by supplying voltage from variac and the temperature can be adjusted by varying the variac voltage also. During CVD process, the temperature of the substrate and the temperature of the activation tungsten heater are measured by optical pyrometer (Brand: Foster, England, Model: AJ/ON/19.5). The process pressure during CVD process is continuously measured by a digital vacuum gauge meter (Brand: vacuubrand, German, Model: VAP 5). The weight of the deposited substrate was measured on a high-resolution weighing scale.

Gas flow inside the reactor chamber during CVD process is measured by a gas flow meter whose range is 0 to 2.0 liter per minute. This flow meter is connected to the supply line of the gas inside the reactor chamber. Natural gas is used as reactant gas for CVD process. The test sample used in this investigation is stainless steel 314. Experimental conditions are shown in table 1. During tests, each experiment was repeated several times and their average results are presented.

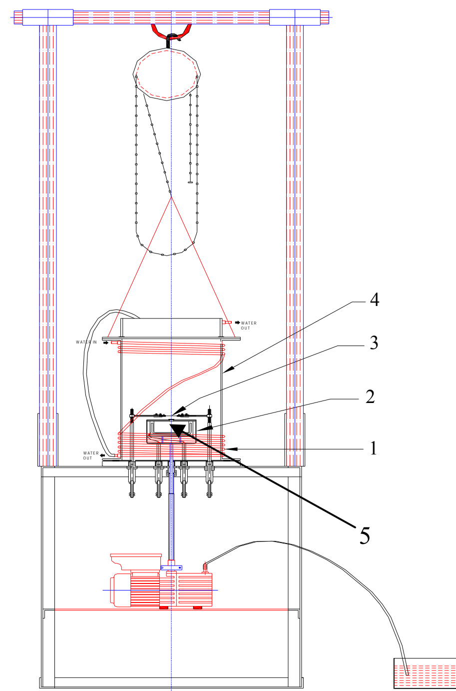

Fig 1. Schematic diagram of chemical vapor deposition (hot filament) setup [1. Cooing tube, 2. Substrate heater, 3. Activation heater, 4. Reactor chamber, 5. Substrate]

Table 1: Experimental Conditions (For CVD)

Sl. no.	Parameters	Range/conditions
1.	Substrate	SS 314
2.	Reactant gas	Natural gas mostly Methane (CH_4)
3.	Substrate thickness	1.5-4mm
4.	Substrate size	20mmX20mm
5.	Distance between activation heater and substrate	4-6.5mm
6.	Flow rate	0.5-2.0 l/min
7.	Pressure	0.085 MPa
8.	Substrate heater temperature	800-1000^0 C
9.	Activation heater temperature	1800-2000^{0}C
8.	Deposition duration	1 hr

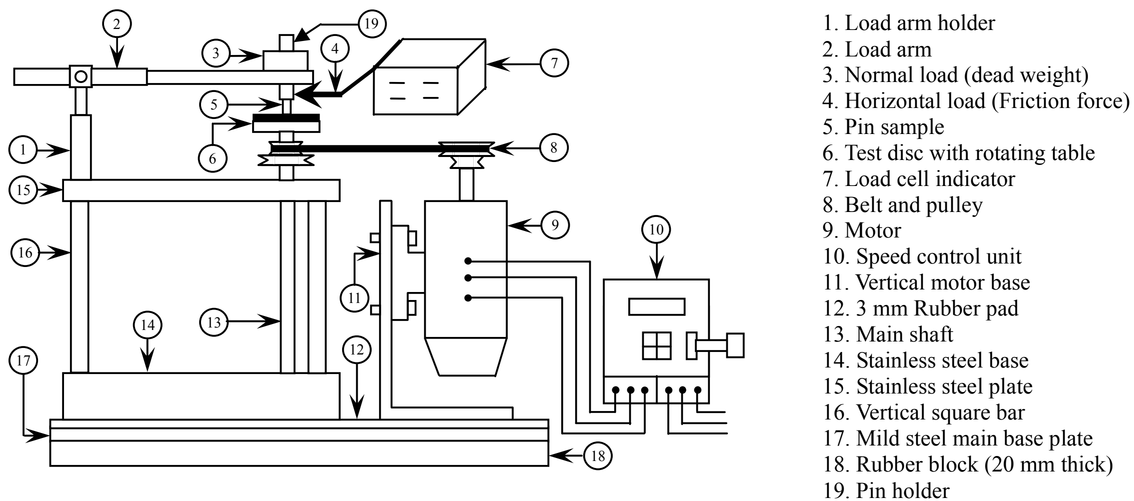

Fig 2. Block Diagram of the Experimental Set-up

2.2 Tribometer for Tribological Test

This is a pin-on-disc machine (Fig.2) i.e. a pin which can slide on a rotating horizontal surface (disc). In this set-up a test sample is to be fixed on a rotating plate (table) having a long vertical shaft clamped with a screw from the bottom surface of the rotating plate.

To rotate the shaft with the table a 1 hp motor is mounted vertically on a separate base having rubber damper. This separate base was arranged to reduce the effect of vibration of the motor, which may transmit to the main structure. An electronic speed control unit is used to vary the speed of the motor as required.

A cylindrical pin whose contacting foot is flat made of SS 304, fitted on a holder is subsequently fitted with an arm. The arm is pivoted with a separate base in such a way that the arm with the pin holder can rotate vertically and horizontally about the pivot point with very low friction. This pin can be put to slide at any point of the test sample (disc). Pin holder is designed with the facility of putting dead weight on it so that required normal force will act on the test sample through the pin. The shape of the pin was maintained cylindrical so that due to loss of surface material of the pin the contacting surface will remain almost constant. To measure the frictional force acting on the pin during sliding on the rotating plate, a load cell (TML, Tokyo Sokki Kenkyujo Co. Ltd, CLS-100NA, Serial no. MR2947) is fitted with a side support such that the load cell prevents the movement of the pin holder. During the rotation of the test sample, pin holder creates pressure on the load cell which gives the measure of the frictional force acting on the pin. Load measuring arrangement was constructed from a separate base to take care the probable fluctuation of friction force that may arise due to the vibration of the test disc. Another load cell of the same kind was also used to measure the vertical force acting on the pin. The coefficient of friction was measured as the ratio between horizontal and vertical forces. Each experiment was carried out for 20 minutes and average values of all these data were considered as friction coefficient. A load cell along with its digital indicator (TML, Tokyo Sokki Kenkyujo Co. Ltd, Model no. TD-93A) was used for measuring loads. The total set-up was placed inside a chamber whose relative humidity can be adjusted by supplying requisite amount of moisture and dehumidifier. A hygrometer (Wet and Dry Bulb Hygrometer, ZEAL, England) was used to measure the relative humidity of the chamber. All experiments were conducted at about 75% relative humidity. A tachometer was used to measure the rpm of the rotating shaft. The surface roughnesses of the test sample were also measured by surface roughness tester (Taylor Hobson Precision Roughness Checker). Wear rates were calculated from the measured weight loss of the disc after rubbing for definite time. Initial and final weights of the disc before and after rubbing were measured on a high-resolution weighing scale. During tests each experiment was repeated several times with new sample of pin and disc.

3. RESULTS AND DISCUSSIONS

3.1. Experimental Results for Deposition Rate

In this study the effects of gas flow rate on deposition rate are investigated at different gaps between activation heater and substrate. The deposition rates are calculated in two ways: (i) the deposition rates of the coating in gram per unit time (mg/min) were calculated from the weight difference of substrate before and after deposition and (ii) the deposition rates of the coating in microns per unit time (μm/min) were calculated from the thickness difference of substrate before and after deposition.

3.1.1 Variation of Deposition Rate (g/min)

Fig. 3 shows the variation of deposition rate (mg/min) on SS 314 with the variation of gas flow rate. Curves 1, 2, 3 and 4 are drawn for gap between activation heater and substrate 6.5, 6, 5.5 and 4 mm respectively. From the curves of this figure it is found that deposition rate increases with the increase of gas flow rate. Results also show that the lower the gap between activation heater and substrate, the higher the values of deposition rate (mg/min) are obtained.

3.1.2 Variation of Deposition Rate (μm/min)

Several experiments are conducted to investigate the effects of gas flow rate on deposition rate (μm/min) and these results are presented in Fig. 4. Curves 1, 2, 3, and 4 of this figure are drawn for gap between activation heater and substrate 6.5, 6, 5.5 and 4 mm respectively. Curve 1 shows that deposition rate increases with the increase of gas flow rate. Similar trends of results are observed for curves 2, 3 and 4. Results also indicate that the lower the gap between activation heater and substrate, the higher the values of deposition rate are obtained.

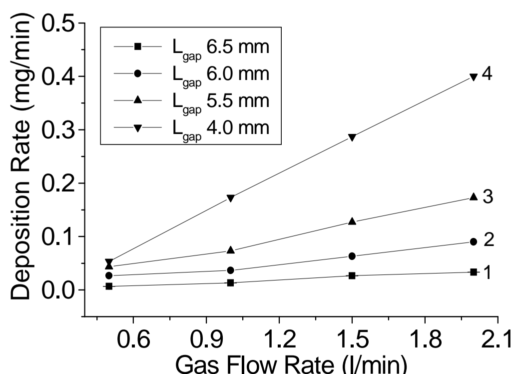

Fig 3. Variation of Deposition Rate (g/min) with the Variation of Gas Flow Rate at Different Gaps between Activation Heater and Substrate for SS 314.

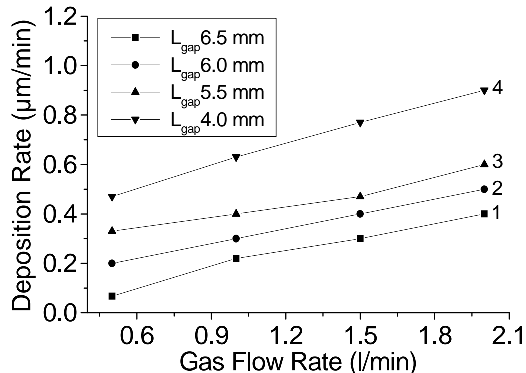

Fig 4. Variation of Deposition Rate (μm/min) with the Variation of Gas Flow Rate at Different Gaps between Activation Heater and Substrate for SS 314.

3.2 Mechanism of Thin Film Growth and Possible Causes of Higher Deposition Rate

The mechanism of thin film growth and the possible causes of deposition with gas flow rate and the gap between activation heater and substrate can be explained as follows:

a) The process of CVD thin film growth can be divided into two steps: (i) the transport of active species and (ii) the incorporation of carbon atoms into the substrate lattice. Under fixed conditions of activating source gases, the production rate of active species is fixed and the thin film growth depends on the rate of the above two steps, that is the transport rate of source gases to the substrate surface and the rate of thin film growth reactions on the growth surface. The surface growth process is controlled by a mass transport process rather than the reaction rate occurring in the growth surface [12, 13]. The direction of gas flow does not influence the thin film growth rate of substrate and growth is affected by the mass diffusion. If the gas flow rate near the growth region is sufficiently strong, convective mass transport will play an important role in thin film growth and gas flow rate markedly affect the growth rate of thin film [12, 13].

b) The complex chemical and physical processes, which occur during CVD, comprise several different but interrelated features. The process gases of the chamber before diffusing toward the substrate surface pass through an activation region (a hot filament), which provides energy to the gaseous species. This activation causes molecules to fragment into reactive radicals and atoms, creates ions and electrons, and heats the gas up to temperatures approaching a few thousand Kelvin. Beyond the activation region, these reactive fragments continue to mix and undergo a complex set of chemical reactions until they strike the substrate surface. At this point the species are adsorbed and entrapped within the surface, some portions are desorbed again back into the gas phase, or diffuse around close to the surface until an appropriate reaction site is found. If a surface reaction occurs, one possible outcome, if all the conditions are suitable, is thin film coating. During this process, the higher the gas flow rate the higher the density of carbon particles is obtained. That is more the density of carbon particle, more amount of deposition on the substrate may be occurred. The increase of deposition rate might be due to elimination or reduction of the local energy barrier during the chemical activity by increasing the gas flow rate.

c) In the case of increased flow rate, higher deposition rates are obtained. One of the conditions required for high deposition rate is that the diffusion of gas toward the substrate is the rate-determining stage. It was considered that the high flow rate made this mechanism possible [17].

d) At high flow rate, diffusion and convection are equally important. While the residence time of the rapid diffusion of atomic hydrogen is not significantly altered, the residence time of heavier carbon-containing species is sensitive to the change in gas flow pattern. The flux of carbon containing species on thin film growth surface is higher at higher flow rate. Celii et al. suggested that the changes of carbon containing species flux with gas flow rates were responsible for the changes in the morphology of the deposited thin films [12, 13].

e) The number of activated carbon species and atomic hydrogen are more near the activation heater [1]. The higher the substrate thickness, the lower the gap between activation heater and substrate are obtained. As the gap between activation heater and substrate reduces, more amounts of activated carbon species may be deposited on substrate and hence increase the deposition rate (coating thickness and weight of deposited materials).

3.3. Comparison of Tribological Behavior before and after Deposition

3.3.1. Surface Roughness

The average roughness of SS 314 before deposition was 0.65 μm. After deposition the average value of roughness becomes 0.50 μm. This indicates smoother surface is obtained after deposition than that of before deposition.

3.3.2. Frictional Behavior

Fig. 5 shows the variation of friction coefficient with the variation of duration of rubbing for SS 314. This figure is drawn for normal load 10-20 N, sliding velocity 1 m/s and relative humidity 75%. At normal load 10 N,

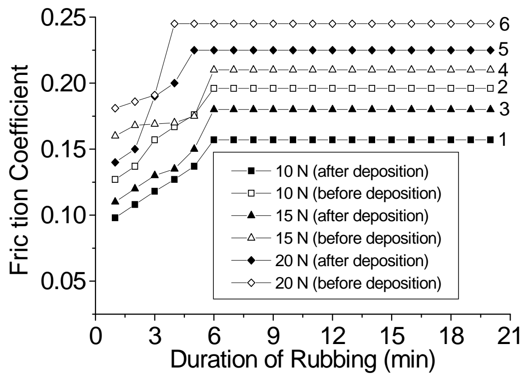

Fig 5. Variation of Friction Coefficient with the Variation of Duration of Rubbing at Different Normal load [Sliding velocity 1 m/s, Relative humidity=75%, Surface roughness before coating 0.65 microns, Surface roughness after coating 0.50 microns, Substrate: SS 314]

curve 1 is drawn for after deposition and curve 2 is drawn for before deposition. It is observed from curve 1 that at initial stage of rubbing, friction coefficient is low (0.098) and then increases almost linearly up to 0.157 and after that it remains constant for the rest of the experimental time. Similarly curve 2 drawn for before deposition shows that at the starting friction coefficient is 0.127 and then increases very steadily up to 0.196 and after that the values of friction coefficient remain almost constant. At starting of experiment the friction force is low due to contact between superficial layer of pin and disc. Then the friction coefficient increases due to ploughing effect and because of roughening of the disc surface. After a certain duration of rubbing, the increase of roughness and other parameters may reach to a certain steady value and for this reason the values of friction coefficient remain constant for the rest of the time. Similar results are obtained for normal load 15 and 20 N i.e. the coefficient of friction is lower for after deposition than that for before deposition. Moreover, the higher the normal load the higher the values of friction coefficient are obtained for before and after deposition. The steady values of friction coefficient at different normal load for after and before deposition are shown in Fig. 6.

3.3.3 Wear Rate

Fig. 7 shows the variation of wear rate with the variation of normal load before and after deposition. Curve drawn for before deposition indicates that wear rate varies from 1.05 mg/min to 1.5 mg/min while for after deposition it varies from 0.5 mg/min to 0.8 mg/min

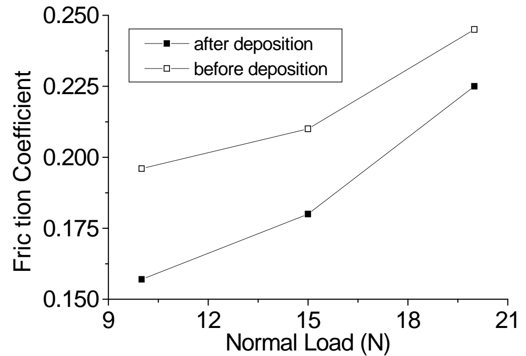

Fig 6. Variation of Friction Coefficient with the Variation of Normal load [Sliding velocity 1 m/s, Relative humidity 75%, Surface roughness before coating 0.65 microns, roughness after coating 0.50 microns, Substrate: SS 314]

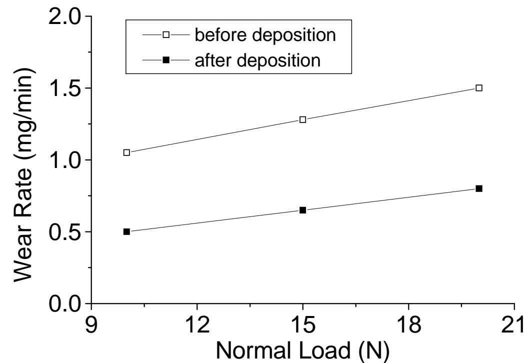

Fig 7. Variation of Wear Rate with the Variation of Normal load [Sliding velocity 1 m/s, Relative humidity 75%, Surface roughness before coating 0.65 microns, roughness after coating 0.50 microns, Substrate: SS 314]

with the variation of normal load from 10 to 20 N. That is the wear rate after deposition is less compared to that for before deposition.

4. CONCLUSIONS

The presence of gas flow rate and gap between activation heater and substrate significantly affect the deposition rate on SS 314. The deposition rate increases with the increase of gas flow rate and it decreases with the increase of gap between activation heater and substrate. The values of friction coefficient, wear rate and surface roughness are lower for deposited condition than that for without deposited condition. Therefore maintaining an appropriate level of gas flow rate and gap between activation heater and substrate, deposition rate may be kept to some optimum value.

5. REFERENCES

1. Huge, O. Pierson., 1999, Handbook of Chemical Vapor Deposition, second edition, Noyes publications, Norwich, New York, U.S.A.
2. Bunshah, R.F., 1994, Handbook of Deposition Technologies for films and Coatings, second edition, Noyes publications, New Jersey, U.S.A.
3. Regel, L.L., and Wilcox, W.R., 2001, “Diamond film Deposited by Chemical Vapor Transport,” Acta Astronautica, 48:129-144.
4. Van der Werf, C.H.M., Goldbach, H..D., Löffler, J., Scarfó, A., Kylner, A.M.C., Stannowski, B., ArnoldBik, W.M., Weeber, A., Rieffe, H., Soppe, W.J., Rath, J.K., Schropp, R.E.I., 2006, “Silicon nitride at high deposition rate by Hot Wire Chemical Vapor Deposition as passivating and antireflection layer on multicrystalline silicon solar cells,” Thin Solid Films, 501:51-54.
5. Stannowski, B., C, H.M., van der Werf., and R, E.I., Schropp., 2000, “Hot-Wire Chemical-Vapour Deposition For Low-Temperature Deposition Of Silicon-NitrideLayers,” Proc. of the 3rd Intern. Conf. on Coatings on Glass, Oct 29 - Nov 2, Maastricht, pp. 387-394.
6. William, N., Shafarman., and Jie, Zhu., 1998, “Effect of Substrate Temperature and Deposition Profile on Evaporated Cu(Inga)Se2 Films And Devices,” paper reference: 0-624 Institute of Energy Conversion University of Delaware, Newark, DE 19716 USA.
7. Corata, E. J., and Goodwin, D. G., 1993, “Temperature dependence of species concentrations near the substrate during diamond chemical vapor deposition”, Journal of Applied Physics, 74:2021-2029.
8. Mark, C., McMaster, I., Wen, L., Hsuap, Michael. E., Coltrin, B., David, S. Dandy., Ciaran Fox, D., 1995, “Dependence of the gas composition in a microwave plasma-assisted diamond chemical vapor deposition reactor on the inlet carbon source: CH, versus & Hz,” Diamond and Related Materials 4:1000-1008.
9. Yongqing Fu., Chang Q., Sun, Hejun Du., Bibo Yan., 2002, “From diamond to crystalline silicon carbonitride: effect of introduction in CH_4/H_2 gas mixture using MW- PECVD,” Surface & coating Technology, 160:165-172.
10. H. Rau, F. Picht, 1992, “Rate limitation in low pressure diamond growth,” Journal of Materials Research, 7:934-939.
11. D.W. Kweon, J.Y. Lee, D. Kim, 1991, “The growth kinetics of diamond films deposited by hot-filament chemical vapor deposition,” Journal of Applied Physics, 69:8329-8335.
12. F.G. Celii, D. White Jr., A.J. Purdes, 1991, “Effect of residence time on microwave plasma chemical vapor deposition of diamond,” Journal of Applied Physics, 70:5636-5646.
13. F.G. Celii, D. White Jr., A.J. Purdes, 1992, “Deposition of smooth, oriented diamond films using microwave plasma chemical vapor deposition,” Thin Solid Films , 212:140-149.
14. J. Yu, R. Huang, L. Wen, C. Shi, 1999, “Nucleation kinetics of diamond in hot filament chemical vapor deposition, Materials Research Bulletin, 34:2319-2325.
15. Q.H. Fan, E. Pereira, J. Cracio, 1999, “Diamond deposition on copper: studies on nucleation, growth, and adhesion behaviours,” Journal of Materials Science, 34:1353-1365.
16. H. Buchkremer-Hermanns, H. Ren, H. Weiβ, 1996, “Optimization of diamond nucleation and growth using MW-PACVD method,” Diamond and Related. Materials, 5:312-316.
17. Kawai, C, 1994, “High-rate deposition of titanium silicides under high gas flow rate by chemical vapor deposition,” Journal of Materials Science Letters, 13:860-862.

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