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LABORATORY EXPERIMENT ON DIAMOND THIN FILM DEPOSITION

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ABSTRACT

A simple deposition system comprising of vacuum and gas delivery systems, and a specimen chamber was designed and constructed to deposit diamond thin films on silicon wafers and tool inserts. The system was used to deposit films with about 25 μm thickness through a hot filament chemical vapor deposition (HFCVD) process. This system is capable of familiarizing students with vacuum and gas delivery systems while providing the opportunity for them to understand and control deposition parameters including substrate temperature, filament distance to sample surface, vacuum level, gas composition, and substrate material effects on the chemical quality of the films deposited. Films characteristics were evaluated using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD). Results indicate that at 90 torr chamber pressure, a high quality of diamond coating was deposited only at substrate temperature above 850°C and CH_4/H_2 ratio less than 2/98. At substrate temperature less than 850°C or CH_4/H_2 ratio higher than 2/98, instead of diamond a layer of diamond-like carbon could be obtained. Optimum distance, d, between filament and substrate at optimized process parameters was found to be 4 mm.

Keywords: *diamond coating, characterization, hot filament chemical vapor deposition, diamond-like carbon, process parameters*

INTRODUCTION

Techniques for deposition of thin diamond films are well established[1]. Transfer of knowledge from research to teaching especially at an undergraduate level seems to be crucial in speeding up advancement of new thin films as well as bulk materials. In this regard, an experimental system was designed and constructed to deposit thin films of diamond on silicon as a laboratory exercise. Diamond film deposition is of interest to semiconductor and manufacturing industries. Diamond shows exceptional physical and mechanical properties including extremely high hardness, high thermal conductivity, high wear resistance, high resistance to many corrosive media, excellent dielectric properties, and is permeable to infra-

red and visible light. The synthesized diamond quickly found its way to market as an abrasive material and in thin film forms for wear resistance applications such as cutting tool inserts. Further research[1] led to deposition of diamond on non-diamond substrates using decomposition of carbon containing gas at lower pressure and moderate temperature of around 1000°C compared to the pressures of above 10^9 Pa and temperature levels of above 2000 °K.

In the present study, a simple setup was assembled to deposit diamond films on Si and WC-Co tool inserts in order to obtain diamond coatings. Since many process parameters effect the deposition properties, several factors including chamber pressure of 90 torr, filament temperature of about 2200°C, and gas flow rate of 200 SCCM were kept constant (Table 1) and other parameters such as substrate temperature, gas composition, and substrate to filament distance were varied. These process parameters were selected based on prior work[2].

Table 1. Process parameters used in deposition of diamond films using hot filament chemical vapor deposition.

Process Parameter	Parameter Range
Substrate temperature (°C)	550-950
Filament temperature (°C)	2200
Vacuum level (torr)	90
Filament-surface-distance (mm)	2-8
Gas chemistry	CH_4 (2-5%) + H_2 (98-95%)
Gas flow rate	200 SCCM

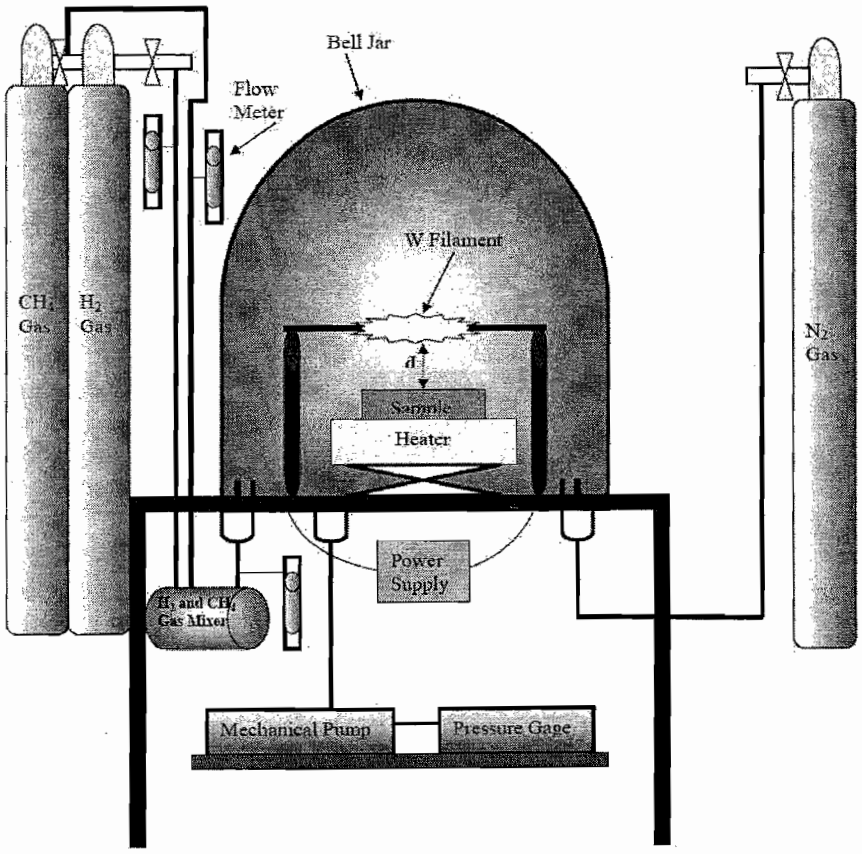

Figure 1. Schematic representation of HFCVD used in this study.

SYSTEM COMPONENTS

A schematic of the simple deposition setup employing in this study is shown in Figure 1. The deposition system is comprised of a bell jar, a mechanical pump, a power supply, gas nozzle (for mixed methane and hydrogen delivery), a thermocouple, and a set of filament coils. A pyrometer to measure filament temperature is recommended but is not a requirement. The chamber pressure was kept at 90 torr for all experiments to minimize contamination. A 0.125 mm diameter of 25 cm length tungsten filament was coiled around a 2 mm metal rod and the filament temperature was also constant at approximately 2200°C (temperature of a glowing hot filament) during the depositions. Two flow meters and a gas mixer were employed in order to obtain various ratios of hydrogen to methane (deposition gas) before delivery to the chamber. The total gas flow rate was kept constant for all experiments at around 200 SCCM (selected based on prior work[2]) using a third flow meter. Figure 1 shows schematic of the gas delivery system used for this deposition system.

EXPERIMENTAL PROCEDURES

In this study three different types of substrate materials including silicon wafer, WC-5%Co, and TiN coated WC-5%Co were used. Silicon wafer specimens were degreased and cleaned using 10% nitric acid to remove contaminants, acetone to degrease the surface, ethyl alcohol to remove acetone residues, and abraded using 0.25μm diamond powder, prior to being placed in the deposition chamber. WC-Co specimens were degreased and cleaned with the same procedure except no abrading was done on them. A Philips X-PERT X-ray diffractometer with Mo-Kα radiation and a Philips XL-30 scanning electron microscope with energy dispersive spectrometer (EDAX) were used to characterize deposited structures. Gas composition was changed and controlled manually through gas inlet valve and gas compositional analysis was done using a Shimatzu gas chromatograph. Surface-to-filament distance was controlled through the use of metallic spacers placed behind the substrate. Table 1 shows range of process parameters used in this research.

RESULTS and DISCUSSION

i) Effect of gas composition and substrate temperature

The first set of experiments was performed at the CH_4/H_2 ratio of 5/95 and various substrate temperatures of Si wafers from 650°C to 950°C. Substrate surface-to-filament distance was kept constant at 4 mm and a heating element was employed to vary the substrate temperature. Micrographs of depositions at 650°C, 750°C, 850°C, and 950°C of substrate temperature were shown in Figure 2. At substrate temperature of 650°C, after 10 hours deposition, a dome like structure appeared on the surface, Figure 2a. Clearly this structure did not have diamond texture. This coating could possibly be considered as one of the varieties of diamond like carbon[4]. When the substrate temperature was increased to 750°C, a cauliflower-like structure was formed, Figure 2b. Another noticeable feature in this deposition was an increasing in the nucleation density of the dome like structure. Further, increase of substrate temperature to 850°C transformed the dome cauliflower-like microstructure to almost spherical crystals shown in Figure 2.c, which were rich in C according to EDS analysis, and grew in size as deposition temperature increased from 650°C to 950°C. Diamond crystals formed at 950°C show a crystal size of about 4 μm as shown in Figure 2.d. According to the results obtained, it became apparent that higher substrate temperatures lead to larger crystals forming. In addition, results of a previous investigation[2] indicated that longer deposition times would yield larger crystals therefore it was decided to use longer deposition time (30 hours) for the remaining experiments.

The X-ray diffraction pattern of the deposited samples compared to the standards patterns of

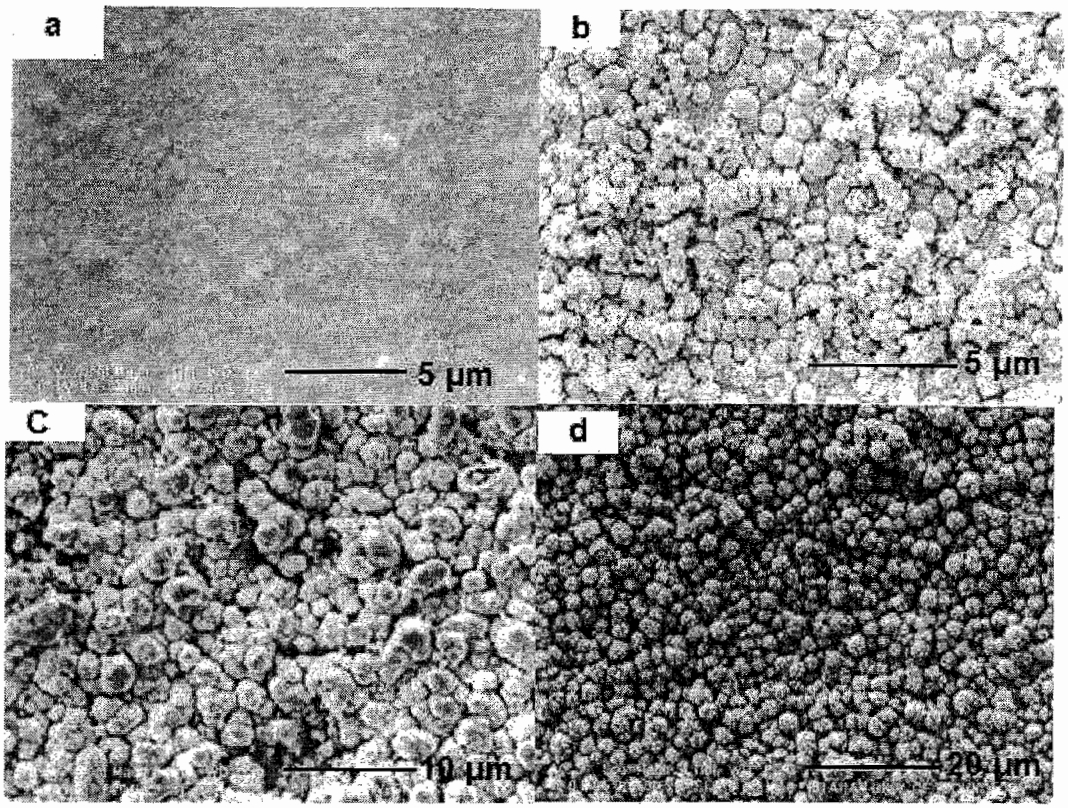

Figure 2. SEM micrographs of films deposited on Si substrate. Chamber pressure= 90 torr, CH_4/H_2=5/95, gas flow rate=200 SCCM, filament temperature=2200°C, deposition time= 10 hours, and substrate temperatures of a) 650°C, b) 750°C, c) 850°C, and d) 950°C.

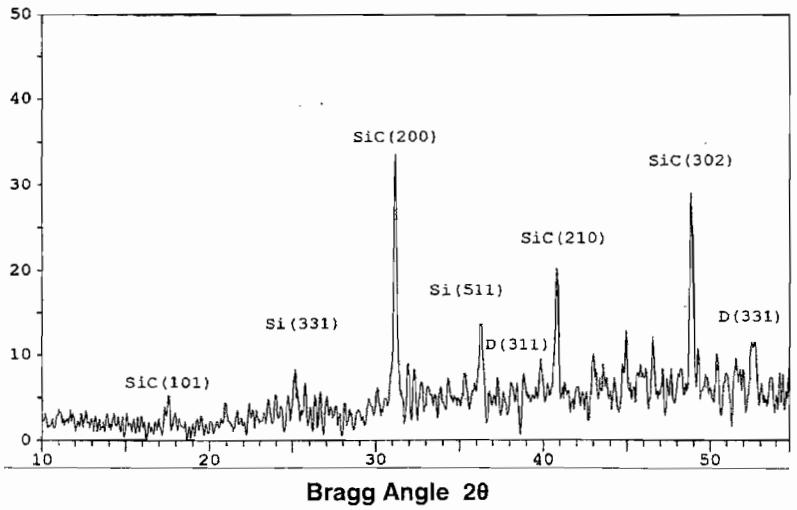

Figure 3. XRD pattern of diamond film coated on Si substrate at 950°C, chamber pressure = 90 torr, CH_4/H_2= 5/95, gas flow rate =200 SCCM, filament temperature =2200 °C.

SiC and diamond shows several reflection peaks related to a SiC layer that apparently formed under the coated material and some small reflection peaks related to diamond as shown in Figure 3. The second set of experiments was performed at the gas ratio of CH_4/H_2 = 2/98 and various substrate temperatures of 650°C, 750°C, 850°C and 950°C for 30 hours. Change of this set of deposition parameters was selected based on the available literature that suggested lower CH_4/H_2 produces better quality diamond films[1,2]. The microstructure formation of deposited layers at various temperatures is shown in Figure 4.

With increasing substrate temperature to 950°C, the morphology of the structure changed toward faceted diamond with the facet planes similar to (111) diamond. At the substrate temperature of 950°C, the morphology of the deposition is definitely diamond structure. The X-ray diffraction pattern of the deposited layer at 950°C for 30 hours is shown in Figure 5. It shows several reflection peaks related to diamond such as (111), (200), (311), and (331) reflections. Because of long time deposition and thus a thicker layer of deposition (~30 μm) on the Si substrate no reflection peak of SiC was detected. EDS analysis shows also only the presence of carbon in the coating.

ii) Effect of surface-to-filament distance

Having optimum substrate temperature, d, (shown in Figure 1) and gas chemical composition, the effect of surface to filament distance from 8 to 2 mm was investigated. At 8 mm distance, morphology of coating was more spherical with no observable facet planes of diamond as shown in Figure 6a. The obtained microstructure was more similar to diamond like carbon. With reducing the distance to 6 mm, (100) and (111) facets of diamond appeared even though some undeveloped grains

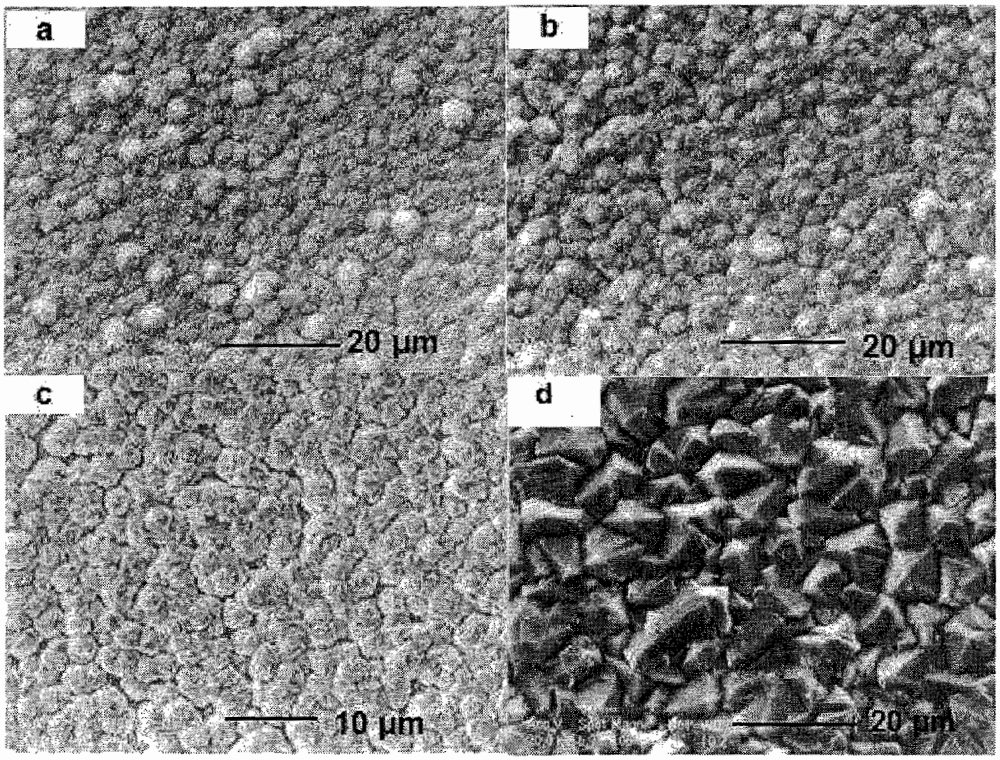

Figure 4. SEM micrographs of diamond films deposited on Si substrate at temperatures of a) 650°C, b) 750°C, c) 850°C, and d) 950°C. Chamber pressure=90 torr, CH_4/H_2=2/98, gas flow rate=200 SCCM, deposition time=30 hours, and filament temperature=2200°C.

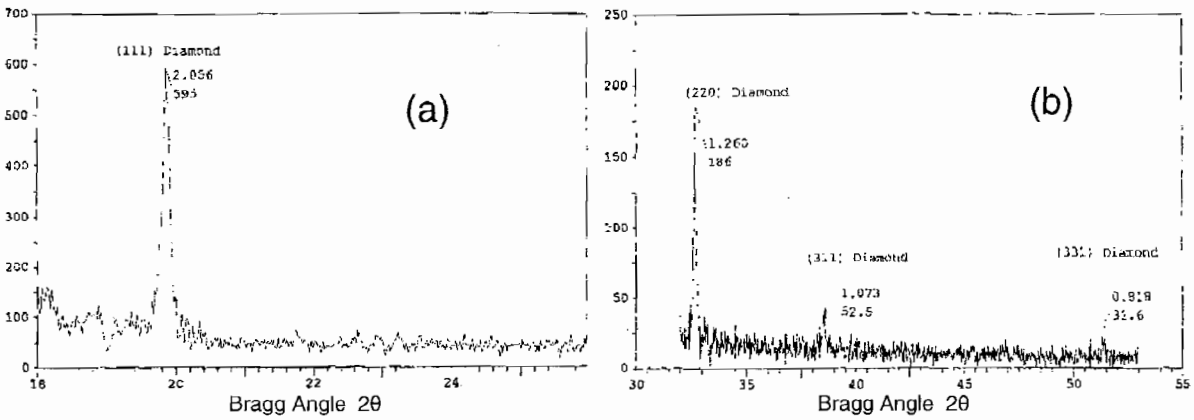

Figure 5. XRD pattern of diamond film coated on Si substrate at 950°C, chamber pressure = 90 torr, CH_4/H_2= 2/98, gas flow rate =200 SCCM, filament temperature =2200 °C. a) 2θ= 18-26° and b) 2θ= 30-55°.

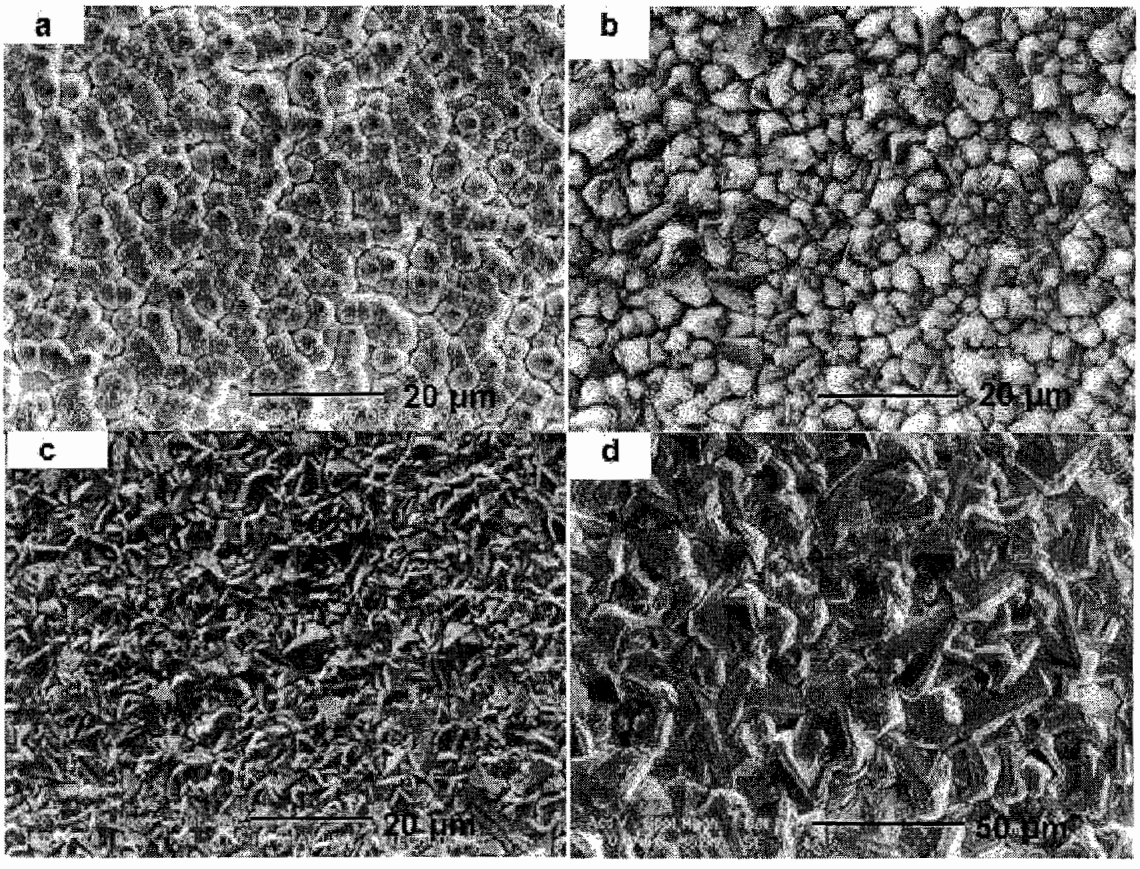

Figure 6. SEM micrographs of diamond films deposited on Si substrate at temperatures of 950°C, chamber pressure=90 torr, CH_4/H_2=2/98, gas flow rate=200 SCCM, filament temperature=2200°C, deposition time=30 hours, and filament to substrate distance of a) 8mm, b) 6mm, c) 4mm, and d) 2mm.

of diamond were present (Figure 6b). Deposited diamond at (4 mm) is shown in Figure 6c. The (100) and (111) facet planes of diamond can be observed clearly in this microstructure. The only explanation for the higher quality of the deposit is due to higher flux from the filament to the surface and therefore higher concentration of atomic hydrogen and hydrocarbon species[1,5-8]. Further reducing the distance to 2 mm decreased the quality of the deposit and caused some diamond like carbon component to form (Figure 6d).

iii) Effect of scratching

As mentioned above the surface of all Si substrates were scratched using 0.25μm diamond powder. Diamond deposition was performed on an unscratched Si sample in order to evaluate the effect of surface scratching on the density of nucleus. By scratching not only the density of surface defects increases (which can act as nuclei sites) but also if scratching is performed using diamond powders, diamond powders can remain inside the defects and on the surface and act as nucleus and therefore enhance the diamond nucleation[1,6]. Figure 7 shows clearly the increased density of diamond nucleation on the scratched surface compared to the unscratched surface under the same deposition conditions.

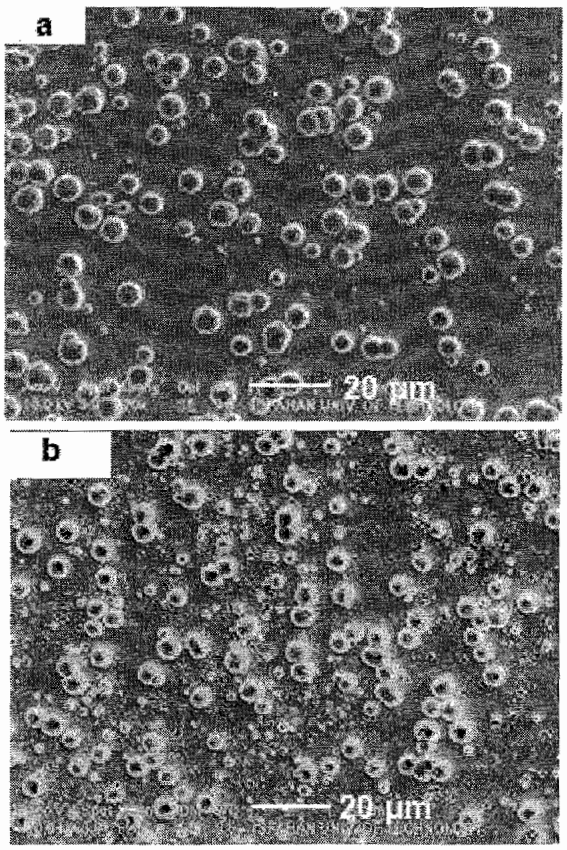

Figure 7. SEM micrographs of prior diamond nucleus formed on Si substrate after 6 hours at temperatures of 950°C, chamber pressure = 90 torr, CH_4/H_2= 2/98, gas flow rate =200 SCCM, and filament temperature = 2200°C. a) Unscratched surface, b) Scratched surface.

iv) Diamond deposition on WC-Co and TiN coated WC-Co

With optimum process parameters for diamond deposition on the Si substrate, WC-Co cutting tool inserts was used as substrates. Micrographs of diamond coatings on the WC-Co (Figure 8 a,b) and WC-Co coated with TiN (Figure 8.c) after 30 hours of deposition are shown in Figure 8. In all microstructures presence of (100) and (111) facets of diamond are obvious. Also average grain size is about 10 μm in both samples. An orthogonal step at a location on the carbide tool (Figure 8b) confirms that diamond deposition could be coated even on the edges of specimen. Cross section of diamond deposition would reveal clearly columnar grain morphology for HFCVD coatings (Figure 8c). Deposition rate in this study was estimated around 1 and 1.2 μm/hr for WC-Co and WC-Co coated with TiN substrates, respectively. The slightly higher deposition rate in the coated samples is due to effect of the TiN intermediate layer in reducing diffusion of atomic carbon into Co[6-8]. TiN can act as an atomic carbon barrier and suppress carbon diffusion into the cobalt substrate. Therefore, the carbon atoms accumulated and supersaturated more rapidly compared to the uncoated carbon.

SUGGESTED EXPERIMENTS

This HFCVD system is capable of depositing diamond films on any metallic or ceramic substrates. Effect of several deposition para-

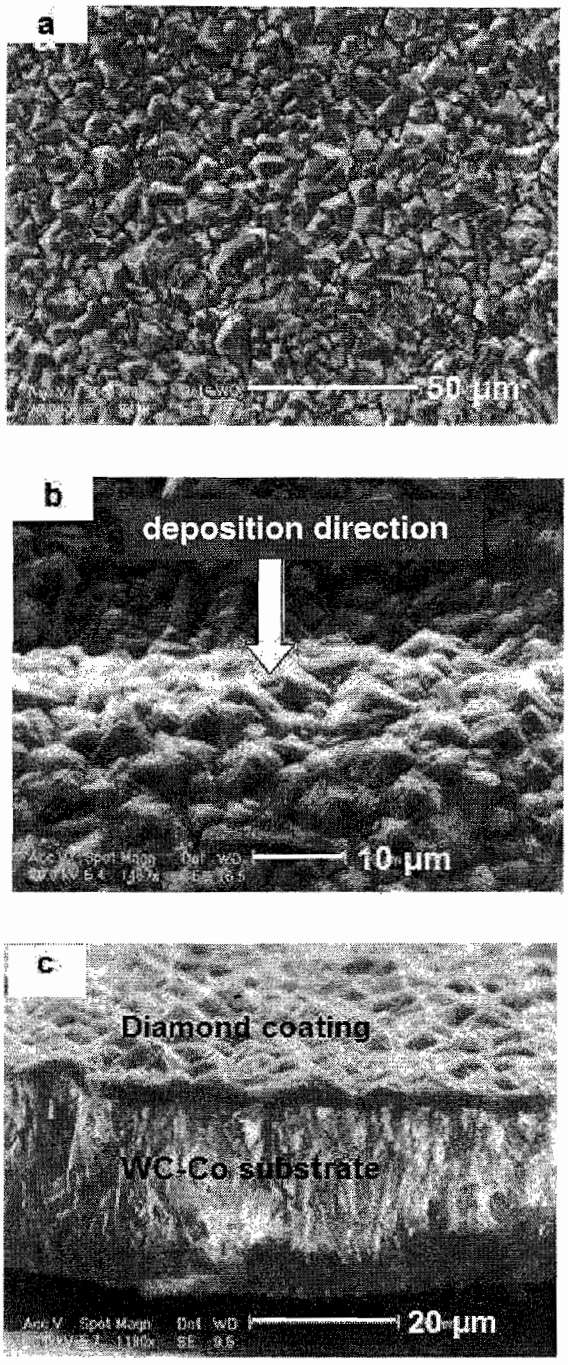

Figure 8. SEM micrographs of diamond films deposited on WC/Co tool insert substrate at temperatures=950°C, chamber pressure=90 torr, CH_4/H_2=2/98, gas flow rate=200 SCCM, deposition time=30 hours, and filament temperature=2200°C. a) WC/Co smooth surface, b) WC/Co orthogonal surface, and c) Cross section of diamond coating on TiN coated WC-Co.

meters (gas chemistry, substrate temperature, filament-to-sample distance, and substrate materials) could be utilized when experimenting on deposited film quality and characteristics. Deposition rates, in terms of film thickness as measured by a scanning electron microscope, can be analyzed. Typical anticipated deposition rates will be about 1 µm per hour. Films' quality, in terms of diamond content, can be characterized using Raman Spectroscopy. Ratio of sp^3/sp^2 bonding in the deposited film determines the film chemical quality[1]. High quality diamond films yield a Raman absorption band centered around 1336 cm^{-1} whereas a graphitic phase results in a 1553 cm^{-1} band in the Raman spectra of a deposited sample[2,8]. Filament- to- sample distance directly affects the flux and collision of hydrogen atoms with the surface, affecting the film quality. It is anticipated a poorer film quality will be obtained at sites further away from the filament.

The educational value of these experiments can be viewed from many different points of view. From the instrumentation point of view, both undergraduates and graduate students could benefit by utilization of mechanical devices including thermocouples, optical pyrometers, pressure gages, and electrical devices such as variable rheostats, power supplies, and multimeters. In addition, this system provides an opportunity for students to learn about gas delivery and vacuum systems. Design and maintenance of a leak proof vacuum system are challenges that all students face when involved with deposition and characterization of materials. This setup provides an opportunity for students to gain experience in working with vacuum systems and learn about pressure measurements, leak detection techniques, and possible solutions in overcoming leakage problems. Results obtained in this investigation should be viewed as a basis of comparison of similar experiments with varying deposition parameters.

Film adhesion to the substrate material is another aspect of diamond deposition on ceramic and metallic substrates. Mismatch in

the coefficient of thermal expansion (CTE) between the diamond film and the substrate often results in film detachment. A possible solution for this issue is to deposit an interlayer film that has an intermediate CTE between both the film and the substrate. The interlayer materials should have specific characteristics, including low carbon solubility in the substrate material at the temperature range (700-950°C), an intermediate value of CTE to reduce thermal stresses, moderate interface reactivity for enhanced adhesion properties, and crystal structure compatible with diamond. This setup can be successfully utilized to undertake inter-layer materials' selection by both undergraduate and graduate students.

CONCLUSIONS

A simple deposition system was employed for diamond coating in this study. The set up provides an opportunity for students to vary process parameters like gas composition, filament-to-surface distance, and substrate temperature as well as substrate materials and surface conditions (e.g. scratched surface *vs.* non-scratched surface) to study effects of those parameters on deposited film quality. Results show formation of high quality diamond coatings on both Si substrate and WC-Co cutting tool inserts. The optimum process parameters for this deposition system were determined to be substrate temperature of 950°C, gas composition of CH_4/H_2= 2/98, gas flow rate of 200 SCCM, filament temperature of 2200°C, and filament-to-substrate distance, d, of 4 mm. Deposition rate on both Si and WC-Co substrates were about 1μm/hr while on the WC-Co coated with TiN samples it was slightly higher at about 1.2μm/hr. Formation of SiC prior to diamond deposition on Si substrate can take place. This SiC layer speeds up diamond formation and also diamond deposition rate due to reduction of the diffusion of atomic carbon into the Si and WC-Co substrates.

A variety of alternative experiments which can be derived from those described in detail here are outlined. They might focus on either the development of instrumentation or tailoring the properties of the deposited films. Thus, the educational value of this primary experiment can be multiplied.

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