Bull. Mater. Sci., Vol. 33, No. 3, June 2010, pp. 251–255. © Indian Academy of Sciences.

Effect of substrate roughness on growth of diamond by hot filament CVD

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MS received 11 July 2008; revised 4 March 2010

Abstract. **Polycrystalline diamond coatings are grown on Si (100) substrate by hot filament CVD technique. We investigate here the effect of substrate roughening on the substrate temperature and methane concentration required to maintain high quality, high growth rate and faceted morphology of the diamond coatings. It has been shown that as we increase the substrate roughness from 0·05 μm to 0·91 μm (centre line average or CLA) there is enhancement in deposited film quality (Raman peak intensity ratio of sp^3 to non-sp^3 content increases from 1·65 to 7·13) and the substrate temperature can be brought down to 640°C without any additional substrate heating. The coatings grown at adverse conditions for sp^3 deposition has cauliflower morphology with nanocrystalline grains and coatings grown under favourable sp^3 condition gives clear faceted grains.**

Keywords. **Hot filament CVD; polycrystalline diamond coating; roughness; morphology; quality.**

1. Introduction

Polycrystalline diamond has excellent mechanical, electrical and optical properties and is chemically inert (Kama *et al* 1983; Narayan *et al* 1992; Gruen 1999; Lee *et al* 1999; May 2000; Das and Singh 2007). To exploit these properties for engineering applications many techniques have been developed in the last three decades to deposit diamond films on engineering components. Hot filament assisted chemical vapour deposition technique (Kama *et al* 1983; Wang *et al* 2003; Sarangi *et al* 2008; Amorim *et al* 2009) is a relatively cheap low temperature process.

One of the main disadvantages of this process is the low growth rate, typically about 1 μm/h (Matsumoto 1982). The growth rate may be enhanced with increased methane ($CH_4 : H_2$) concentration but at the cost of film quality (Kama *et al* 1983; Narayan *et al* 1992); the morphology of the film degrades from a cubic facetted to a cauliflower or a spherical structure (Kobashi *et al* 1990). Takahashi *et al* (2002) have shown that increasing the methane concentration from 0·5% increases the adhesive toughness of the film as the crystal changes its phase from monocrystalline to polycrystalline with a reduction in grain size. The mechanical property, however, deteriorates at high methane concentration of 5% as the grain size becomes very small (cauliflower morphology). The quality may, however, be improved by increasing the process temperature (Kondoh *et al* 1994), but this of course increases the cost.

Growth of diamond begins when individual carbon atoms nucleate onto the surface in such a way as to initiate the beginnings of an sp^3 tetrahedral lattice. When using natural diamond substrates (a process called homoepitaxial growth), the template for the required tetrahedral structure is already present, and the diamond lattice is just extended atom-by-atom as deposition proceeds. But for non-diamond substrates (heteroepitaxial growth), there is no such template for the C atoms to follow, and those C atoms that deposit in non-diamond forms are immediately etched back into the gas phase by reaction with atomic H. As a result, the initial induction period before which diamond starts to grow can be prohibitively long (hours or even days). Growth of diamond films on a foreign substrate using a CVD process typically requires surface treatment in order to achieve a high nucleation density (Butler and Sumant 2008). To combat this problem, the substrate surface often undergoes a pre-treatment prior to deposition in order to reduce the induction time for nucleation and to increase the density of nucleation sites. This pre-treatment can involve a number of different processes. The simplest is abrasion of the substrate (Lee

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et al 1999) surface by mechanical polishing using diamond grit ranging in size from 10 nm–10 μm. The sample preparation techniques used for nucleation enhancement include scratching by diamond powder or any other abrasive (Mitsuda *et al* 1987; Chang *et al* 1988; Suzulu *et al* 1995), pre-deposition of interlayer (Feng *et al* 1993), seeding the substrate with diamond grit (Jansen *et al* 1990), electrical biasing of the substrates (Stoner *et al* 1992) and ion implantation of substrate surface (Hirabayashi *et al* 1988; Lin *et al* 1992). Among these, mechanical abrasion of substrate surface has proved most effective and cheapest. It has been employed for almost two decades of seeding the substrate with diamond particles through the use of a slurry of diamond particles dispersed in an appropriate solvent like alcohol, acetone etc and accompanied by ultrasonic agitation. With recent advent of detonated nanodiamond (DND) technology, it is very efficient to increase nucleation density and its uniformity using DND slurries for substrate scratching (Shenderova *et al* 2010). It is suggested that during agitation/scratching by abrasive material, residual powder or fragments are unavoidably left in the scratched groove and these act as seeds for diamond growth (Chang *et al* 1988; Suzulu *et al* 1995; Lee *et al* 1999). An alternative mechanism (Chang *et al* 1988; Suzulu *et al* 1995; Lee *et al* 1999) is that scratching with powder creates a change in the surface morphology, such as edges, steps, dislocations and other surface defects. These kinds of defects are labeled chemically active sites, which prefer to adsorb diamond precursors together due to enhanced bonding at high energy intersecting surfaces with a high density of unsaturated bonds and low coordination numbers. An order of 30 nm of substrate roughness created by mechanical abrasion has been found useful (Popovici *et al* 1992) for this purpose.

We have in this work investigated the effect of substrate roughness on the growth rate and coating quality with an aim to optimize process temperature and methane concentration. We deposited diamond in a hot filament reactor on 0·5 mm thick Si (single crystal) wafers. We have found that substrate roughening enables the lowering of process temperature and increase of methane concentration without impairing coating quality.

2. Experimental

A conventional hot filament chemical vapour deposition (HFCVD) reactor (figure 1) was used to deposit diamond on silicon substrates. The substrate heater consisted of a high purity alumina casing, holding a 0·5 mm thick (6 turns) tungsten filament. The casing was placed on a steel holder which held the substrate on top of the heater casing. The substrate used here was *n*-type Si (100) wafer of 0·5 mm thickness. The substrates were scratched using 1–3 μm diamond paste by ultrasonic method. The scratched substrates were rinsed in acetone, alcohol, dilute hydrofluoric acid solution and then washed in distilled water and dried before being placed on the alumina casing of the substrate heater.

The deposition chamber was evacuated to a pressure of 50×10^{-3} mbar. The hydrogen was bled into the chamber at 200 sccm (standard cubic centimeter per minute). The filament was heated to 2000°C monitored by a two-wavelength optical pyrometer (MIKRON). The substrate temperature was controlled using a thermocouple and a feed back temperature-controller. Once the temperature was stabilized, methane was bled at a flow rate of 200 sccm using a mass flow controller (Bronkhorst Hi-Tec, EL-Flow). The methane gas decomposed into radicals and the hydrogen gas split into atomic hydrogen to react at the substrate surfaces (Butler and Woodin 1993) and grew into tetrahedral diamond. The flow of methane, substrate temperature and the deposition time were varied in the study. Raman spectroscopy was done to monitor quality of the deposit. The Raman experiments were performed in a 90° geometry using a Jobin Yvon Triax 550 tripple grating spectrometer equipped with cryogenic charge-coupled device camera, using diode-pumped frequency doubled solid state Nd–YAG laser of 532 nm (Model DPSS 532–400, Coherent Inc.). A super notch filter was used to eliminate the Rayleigh scattering. The deposited specimen was broken, polished and the cross section viewed in the scanning electron microscope to measure the film thickness. A profilometer (Taylor and Hobson, Talysurf) was used to measure the roughness of the surface, here we report the centre line average (CLA). The grain size of the deposited film was measured using an AFM (Explorer™, Veeco Instruments Inc.) in the contact mode.

3. Results and discussion

An unscratched silicon wafer has characteristic roughnesses of the orders of 0·025 μm (CLA) and 0·69 μm

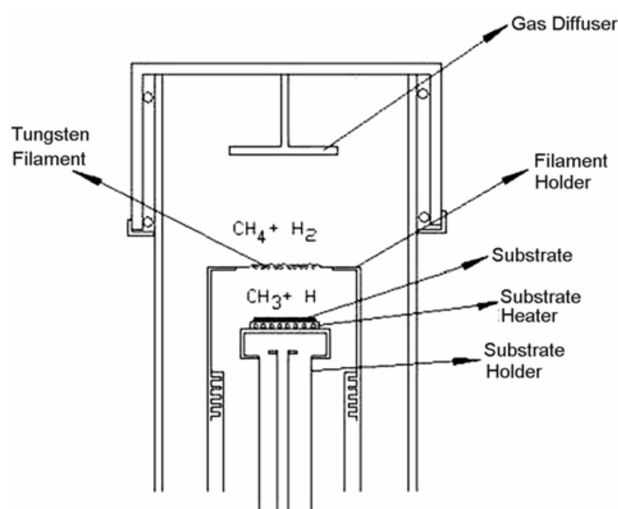

Figure 1. Schematic of HFCVD reactor.

(CLA) on the two opposite faces. Scratching both faces yielded roughnesses of the orders of 0·045 μm (CLA) and 0·988 μm (CLA), respectively.

Our results show that the coating thickness (≈ 6 μm) does not vary significantly with the substrate roughness but the morphology of the coating varies considerably. The coatings grown (2% methane concentration, 750°C substrate temperature) on the smooth (scratched) substrate (≈ 0·045 μm, CLA) has distinct cauliflower

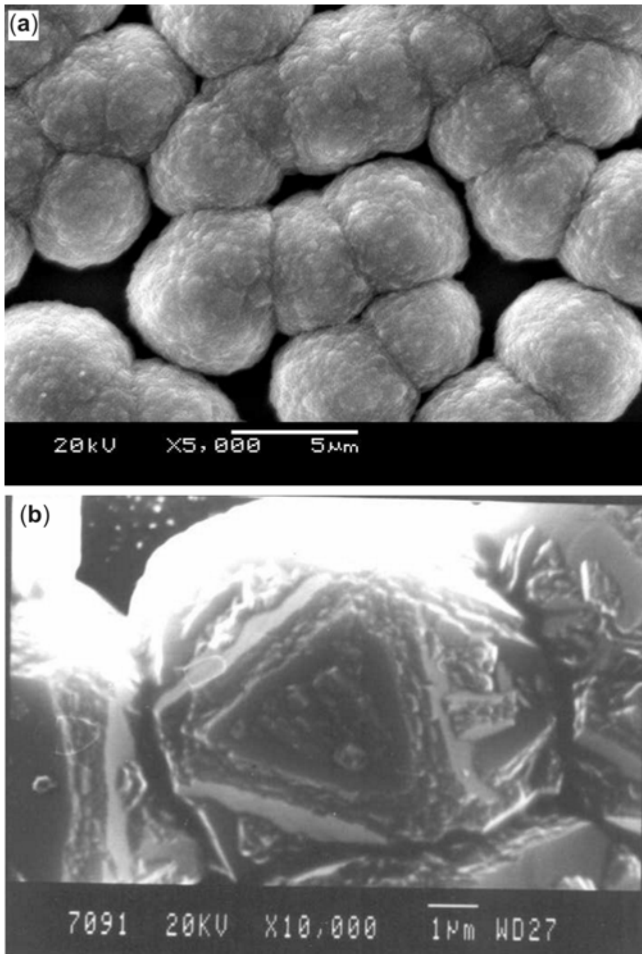

Figure 2. Morphology of diamond coatings grown on Si (100) substrates, CH_4 concentration, 2%; substrate temperature, 750°C: (**a**) smooth substrate, showing cauliflower morphology and (**b**) rough substrate, showing faceted morphology.

Table 1. Effect of substrate roughness on morphology of diamond coating.

Roughness	Morphology	Methane concentration (%)	Substrate temperature
Smooth (0·045 μm)	Cauliflower	2	750°C
Rough (0·988 μm)	Faceted	2	750°C
Smooth (0·045 μm)	Faceted	2	800°C
Rough (0·988 μm)	Cauliflower	2	700°C

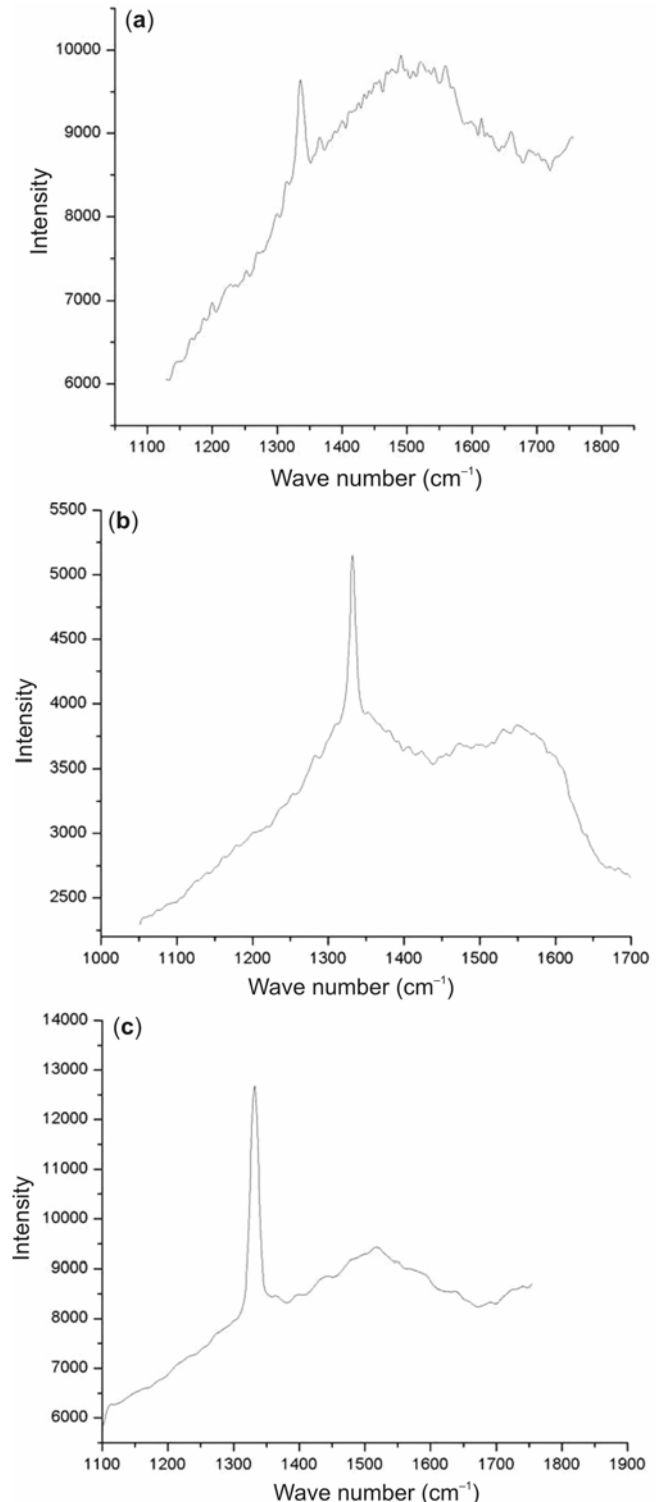

Figure 3. Raman spectra of diamond coating grown on Si(100) substrate: (a) substrate roughness, 0·05 μm CLA; substrate temperature, 950°C; methane concentration, 1·5%, (b) substrate roughness, 0·85 μm CLA; substrate temperature, 810°C; methane concentration, 1·5% and (c) substrate roughness, 0·91 μm CLA; substrate temperature, 900°C; methane concentration, 3%.

Table 2. Effects of process parameters and substrate preparation on the quality of diamond coating.

Row	Figure no.	$CH_4:H_2$ (%)	Substrate temperature (°C)	Substrate heater	Substrate roughness	Coating thickness (μm)	Growth rate (μm/h)	Peak position	FWHM	Integrated peak intensity, 1332 cm^{-1} (I_d)	Integrated peak intensity, 1500–1600 cm^{-1} (I_g)	Intensity ratio (I_d/I_g)
1	Figure 3a	1·5	950	Yes	Smooth	6·57	1·09	1333·9	12·9	1290·78	778	1·65
2	Figure 3b	1·5	810	Yes	Rough	5·12	0·84	1331·59	10·526	5435	944	5·75
3	Figure 3c	3	900	Yes	Rough	5·93	0·97	1332·28	8·488	1533	215	7·13
4	–	2	640	No	Smooth	0	0	–	–	–	–	–
5	Figure 4	2	640	No	Rough	5·92	0·97	1331·62	13·71	3327	762	4·36

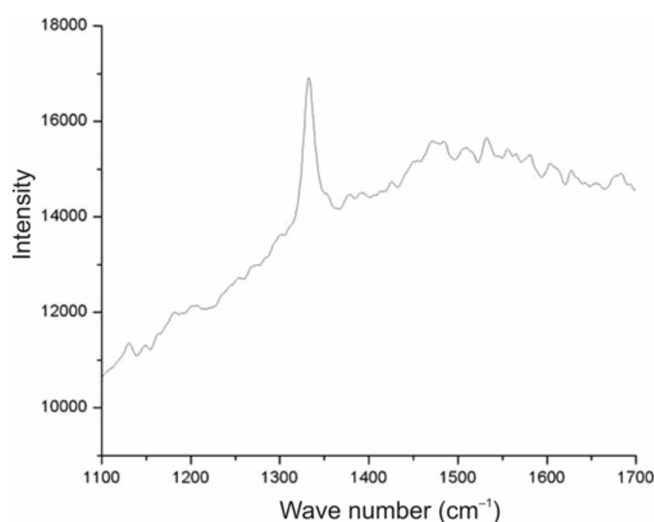

Figure 4. Raman spectra of diamond coating grown without the use of a substrate heater, substrate roughness, 0·94 μm CLA; substrate temperature, 640°C; methane concentration, 2%.

morphology (figure 2a) with grain size in the 100–200 nm range. The coating grown (2% methane concentration, 750°C substrate temperature) on the rough substrate (1 μm CLA) showed clear faceted morphology (figure 2b, table 1) with grain size in the 3–5 μm range. Increasing the temperature of the smooth substrate to 800°C, however, yielded a faceted morphology of the diamond coating. We could obtain continuous films at low temperatures (640–700°C) only when the methane concentration was more than 2% but the substrate face in such cases had always to be rough. The only disadvantage we could observe in attempting to manipulate surface morphology using roughness as a parameter was that not only did the faceted morphology showed higher (0·5–0·6 μm, CLA) roughness than the cauliflower morphology (0·25–0·45 μm, CLA) but the same morphology obtained on a rough substrate showed a higher roughness than that obtained on a smoother substrate.

Figure 3a shows the Raman spectrum of a coating (thickness, 6·75 μm) deposited on a scratched smooth surface of a silicon wafer. The peak at 1332 cm^{-1} is characteristic of C tetrahedral whereas the hump at 1500–1600 cm^{-1} is a characteristic of graphite. We mark the (diamond peak) coating quality by the ratio of the intensity of the peak to hump, the higher the 1332 cm^{-1} peak and lower the 1500–1600 cm^{-1} hump intensity we infer an enhancement of coating quality. Table 2 summarizes the key experimental results. It is well established (Kondoh *et al* 1994) that decreasing the substrate temperature deteriorates the coating quality. By comparing rows 1 and 2 (table 2), we, however, observe that the methane concentration remaining the same, it is possible to suppress this effect (due to reduction of substrate temperature by 140°C) completely and improve the coating quality 3·5 times (compare intensity ratio and also see figure 3b) by making the 'lower temperature' substrate rough. The cost of doing this is a lowering of coating growth rate (by 20%) and an enhancement of coating roughness from 0·1 μm (CLA) to 0·22 μm (CLA).

A similar result is obtained by increasing the methane concentration. It is known (Kobashi *et al* 1990) that increasing methane concentration deteriorates the coating quality but increases the growth rate. By comparing rows 1 and 3 in table 2 and figures 3a and 3c, it is clearly seen that this tendency for deterioration of coating quality is completely superceded by the 'roughness' effect and coating quality improves several times. This unfortunately happens at the cost of neutralizing the expected increase in growth rate due to an increase in methane concentration.

We next decrease the substrate temperature by removing the substrate heater. We found the growth to be discontinuous when the deposition was done on the smooth substrate (row 4, table 2). Roughening the substrate, however, produced a high quality coating (row 5, table 2, figure 4) even at a substrate temperature as low as 640°C.

The substrate roughness effect on diamond growth can be explained as follows: it is a well known fact that nucleation of diamond requires seeding the substrate with diamond (Chang *et al* 1988; Jansen *et al* 1990; Suzulu *et al* 1995; Lee *et al* 1999). As we have scratched the

substrate with 1–3 micron diamond paste before deposition in ultrasonic bath, the bare substrates got roughened and the diamond particles in the paste got stuck in the valleys of the roughened surface. As the depth of valley increases with surface roughness, more diamond particles get embedded within the asperities and troughs of the surface. This enhances nucleation of the diamond crystal and its growth behaviour.

4. Conclusions

The substrate roughness is shown here to have a strong effect on the morphology and quality of diamond coatings grown on Si (100) substrate by hot filament CVD technique. Increasing the substrate roughness encourages faceted morphology and improves coating quality. We conclude that roughening of the substrate allows the lowering of substrate temperature and enhancement of methane concentration, both practices favoured for the reduction of cost of production of polycrystalline diamond coating, without compromising on the quality and nature of the coating.

Acknowledgements

The authors thank the Indian Space Research Organization for financial support and the CTI, BHEL, for making available deposition facilities.

References

Amorim A, Nascente P A P, Trava-Airoldi V J, Corat E J, Alves A R and Moro J R 2009 *Vacuum* **83** 1054

Butler J E and Woodin R L 1993 *Philos. Trans. R. Soc. London* **A342** 209

Butler J E and Sumant A V 2008 *Chem. Vap. Depos.* **14** 145

Chang C P, Flamn D L, Ibbotson D E and Mucha J A 1988 *J. Appl. Phys.* **63** 1744

Das D and Singh R N 2007 *Int. Mater. Rev.* **52** 29

Gruen Dieter M 1999 *Ann. Rev. Mater. Sci.* **29** 211

Feng Z, Komvipoulos K, Brown I G and Bogy D B 1993 *J. Appl. Phys.* **74** 2841

Hirabayashi K *et al* 1988 *Appl. Phys. Lett.* **53** 1815

Jansen F, Machonkin M A and Kuhman D E 1990 *J. Vac. Sci. Technol.* **A8** 3785

Kama M, Sato Y, Matsumoto S and Setaha N 1983 *J. Cryst. Growth* **62** 642

Kobashi K, Nishimura K, Miyata K, Kumagai K and Nakaue A 1990 *J. Mater. Res.* **5** 2469

Kondoh K, Ohta T, Mitomo T and Ohtsuka K 1994 *Diam. Rel. Mater.* **3** 270

Lee S T, Lin Z and Jiang X 1999 *Mater. Sci. & Eng.* **R25** 123

Lin S J *et al* 1992 *Appl. Phys. Lett.* **60** 1559

Matsumoto S 1982 *J. Mater. Sci.* **17** 3106

Mitsuda K, Kojima Y, Yoshida T and Akashi K 1987 *J. Mater. Sci.* **22** 1557

Narayan J, Godbole V P, Matera G and Singh R K 1992 *J. Appl. Phys.* **71** 966

May Paul W 2000 *Philos. Trans. R. Soc. London* **A358** 473

Popovici Galina and Prelas M A 1992 *Phys. Status Solidi* **132** 233

Sarangi S K, Chattopadhyay A and Chattopadhyay A K 2008 *Appl. Surf. Sci.* **254** 3721

Shenderova O, Hens S and McGuire G 2010 *Dia. Rel. Mater.* **19** 260

Stoner B R, Ma G H M, Wolter S D and Glass J T 1992 *Phys. Rev.* **B45** 11067

Suzulu K, Swabe A, Yasuda H and Inuzuka T 1995 *Appl. Phys. Lett.* **66** 1900

Takahashi H, Kamiya S and Saka M 2002 *J. Am. Ceram. Soc.* **85** 179

Wang A, Sun C, Huang R, Wen L, Cailiao Kexue and Yu Jishu 2003 *J. Mater. Sci. & Technol., China, USA* **19** 22