Structure of diamond and diamond like carbon thin films grown by hot-filament chemical vapour deposition technique[†]

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Abstract. Micro-crystalline diamond (MCD) and diamond like carbon (DLC) thin films were deposited on silicon (100) substrates by hot-filament CVD process using a mixture of CH₄ and H₂ gases at substrate temperature between 400–800°C. The microstructure of the films were studied by X-ray diffraction and scanning electron microscopy. The low temperature deposited films were found to have a mixture of amorphous and crystalline phases. At high temperatures (> 750°C) only crystalline diamond phase was obtained. Scanning electron micrographs showed faceted microcrystals of sizes up to 2 µm with fairly uniform size distribution. The structure of DLC films was studied by spectroscopic ellipsometry technique. An estimate of the amount of carbon bonds existing in sp^2 and sp^3 form was obtained by a specially developed modelling technique. The typical values of sp^3/sp^2 ratio in our films are between 1.88–8.02.

Keywords. Diamond; carbon; chemical vapour deposition; ellipsometry.

1. Introduction

Diamond, being an excellent material for various electronic, wear protective, thermal and optical applications has become one of the most studied and strategic materials (Deshpandey and Bunshah 1989). Its large number of applications stem from its unique and excellent properties which arise due to the strong covalent C–C bonding between its constituent atoms. Synthetic diamond films are produced mainly by chemical vapour deposition (CVD) methods by decomposition of hydrocarbon gases. The films have particles which often appear as octahedral, cubo-octahedral or multiply twinned particles according to the deposition conditions (Matsumoto and Matsui 1983; Matsumoto 1985; Kim *et al* 1990). On the other hand DLC films are predominantly amorphous with varying amounts of sp^3 and sp^2 coordinated carbon atoms in a random network.

The desire to understand the properties of these films has stimulated a number of structural investigations and attempts at modelling the microstructure of DLC matrix (Stenhouse and Grant 1978; Fink *et al* 1983; Beeman *et al* 1984; Savvides 1985). The structure and morphology of these films are crucially dependent on the parameters employed for deposition. An accurate control over these parameters is, therefore, absolutely essential.

We have employed a hot-filament CVD technique to grow good quality micro-crystalline diamond and DLC films. The advantages of this technique over other CVD techniques are described elsewhere (Deshpandey and Bunshah 1989). The films have been characterized for structure, morphology and various carbon phases by X-ray diffraction, SEM and spectroscopic ellipsometry techniques. The real and imaginary

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parts of the dielectric constant were used to model the amount of sp^3 and sp^2 coordinated carbon atoms in DLC films by use of Kramer–Kronig relations as applied to a specially developed modelling technique.

2. Experimental

The hot-filament CVD set-up used for deposition of diamond/DLC films is shown in figure 1. We used a 0.25 mm tungsten wire coil held at temperatures $> 2000^\circ\text{C}$ for the decomposition of the incoming gases. The temperature of the substrates, which were placed in the close vicinity of the filament, increased substantially by radiation. Additional heat was provided by the second filament placed below the substrate. This assisted in obtaining an independent control of the substrate temperature. A mixture of CH_4 and H_2 was used as the source gas and released from a single nozzle placed above the filament. The films were deposited on p -type single crystal Si(100) substrates. The substrates were pretreated by scratching with $0.5\ \mu\text{m}$ diamond paste and later ultrasonically treated in a diamond powder suspension. This causes cavitation erosion of the

Figure 1. Schematic set-up of hot-filament CVD system used for the present work.

Table 1. Typical deposition parameters used to grow diamond and diamond like carbon thin films.

Parameter	Diamond films	DLC films
Source gases	$\text{CH}_4 + \text{H}_2$	$\text{CH}_4 + \text{H}_2$
Filament temperature	$> 2000^\circ\text{C}$	$> 2000^\circ\text{C}$
Substrate temperature	$750\text{--}800^\circ\text{C}$	$400\text{--}700^\circ\text{C}$
Working pressure	10–50 Torr	1–30 Torr
Total gas flow	150–200 sccm	150–200 sccm
Gas ratio ($\text{CH}_4:\text{H}_2$)	1:5:130–1:5:90	1:10–1:100
Substrate	Si(100) p -type	Si(100) p -type

substrate surface and thus provides low free energy sites for a faster rate of nucleation. The substrates were then degreased and cleaned in trichloroethylene and acetone ultrasonically. The typical deposition parameters are as given in table 1.

3. Results and discussion

Figures 2a and b show the glancing angle X-ray diffraction patterns for diamond and DLC films respectively. Figure 2a shows the presence of (111) and (220) orientations of the polycrystalline diamond phase. No amorphous phase was observed within the limits of the experiment. Figure 2b shows a broad amorphous feature. Figures 3a–c show the SEM micrographs of these films. The micrographs for diamond films showed both rounded as well as well faceted micro-crystallites in the films. The crystallite morphology of the diamond films during growth was highly sensitive to the growth conditions and reflected the growth mechanism. The micrographs showed that

Figure 2. a. X-ray diffraction pattern of a typical micro-crystalline diamond film and b. X-ray diffraction pattern of a typical DLC film.

Figure 3. Scanning electron micrographs of diamond thin films: **a.** diamond thin film at initial stages of growth, **b.** diamond thin film of **a** at later stages of growth and **c.** film deposited at lower CH₄/H₂ ratio showing faceted growth of diamond micro-crystallites.

rounded crystallites were essentially diamond polyhedra with very large number of faces which gave the rounded look. These shapes were observed only in films prepared with a very high CH_4/H_2 flow ratio. This may be due to lower rates of etching of amorphous and non-diamond phases being deposited along with the diamond micro-crystallites. This results in incorporation of defects and $\text{C}=\text{C}$ bonds in addition to the sp^3 hybridized covalent bonds. On the other hand, by increasing the hydrogen concentration the non-diamond carbon was removed and the active species reaching the substrate surface oriented themselves into tetrahedral configuration before forming the saturated covalent bonds with the growing film. Thus we obtained well faceted crystallites with defects incorporated only at the grain boundaries. The films were $1.5\text{--}2.0\text{ }\mu\text{m}$ thick as measured with the 'Talystep'. The average particle size was about $1.5\text{ }\mu\text{m}$ as observed from the SEM micrographs.

Figure 4 shows the variation of real and imaginary parts of the dielectric constant of the diamond film. ϵ_1 variation shows no special feature in the range (1.5–5.0 eV) of the experiment. This is a characteristic feature of the diamond phase. In addition, ϵ_1 remains positive throughout the spectral range showing the absence of any graphitic phase. The ϵ_2 variation is directly related to the interband transitions. The $\sigma\text{--}\sigma^*$ transitions in diamond occur after 7 eV whereas graphitic carbon gives structure in ϵ_2 at 4.8 eV. The ϵ_2 spectrum shows no structure around 4.8 eV which indicates the absence of graphite phase in our films. The 7 eV structure could not be observed as it was much beyond the range of the instrument. Figure 5 shows the typical ϵ_1 and ϵ_2 spectra of a DLC thin film. The spectra show larger spectral dependence and higher absorption as compared to that shown in figure 4. The structure in ϵ_2 spectrum near 3.0 eV is a characteristic feature of amorphous carbon phase.

A modelling technique has been developed to estimate the sp^3/sp^2 ratio in our films by using experimentally observed ellipsometric data. In this method, the effective

Figure 4. ϵ_1 and ϵ_2 variation of a diamond thin film in 1.5–5.0 eV energy range.

number of π electrons/carbon atom were calculated from the ϵ_2 obtained by gaussian fit (Demicheles and Pirri 1992; Wemple and Didomenico 1971) to the experimentally determined ϵ_2 data. A void fraction of 20% and hydrogen concentration of 25% in the DLC films has been assumed and these values have been used to calculate the total number of electrons/unit volume in the DLC matrix. The detailed method is described elsewhere (Sah *et al* 1996).

The typical values obtained for our films varied from 1.88–8.02 depending on the deposition conditions as shown in table 2.

Table 2 shows that the sp^3/sp^2 ratio for films deposited at higher pressure was lesser than for the films deposited at lower pressures. The films deposited at higher pressures tended to have more graphitic carbon atoms than those deposited at lower working pressures. Similar results have been observed with films prepared using C_2H_2 as the source gas (Sah *et al* 1996). This may be because the mean free path of the active radical species produced by decomposition of the hydrocarbon gas decreases as the working pressure increases. This leads to lower supersaturation of active radical species near the substrate surface although the supersaturation of the various gas species increases. Consequently, the amount of sp^3 coordinated carbon atoms decreases. The amount of hydrogen in the source gases also influences $Csp^3:Csp^2$ ratio by increasing/decreasing

Figure 5. ϵ_1 and ϵ_2 variation of a DLC film in 1.5–5.0 eV energy range.

Table 2. Dependence on deposition parameters of sp^3/sp^2 ratios obtained for DLC films.

Sample name	sp^3/sp^2 ratio	Source gas	Hydrocarbon/ H_2 ratio	Substrate temp.	Pressure (torr)
M1	1.88	CH_4	2.5:100	800°C	30
M2	8.02	CH_4	5:70	750°C	10

the passivation of dangling bonds on the surface and in the bulk of the DLC matrix. It has been observed that higher hydrogen concentrations lead to higher sp^3/sp^2 ratios.

4. Conclusions

Good quality microcrystalline diamond thin films have been deposited on Si(100) single crystal pretreated substrates. The crystallite morphology and growth rates have been studied with respect to the deposition parameters. Consequently, deposition parameters have been optimized to obtain the required crystalline quality. Using the experimentally determined real and imaginary parts of dielectric constants, a theoretical model has been used to estimate the ratio of sp^3/sp^2 coordinated carbon atoms in DLC films. The results have been correlated to the deposition parameters employed. It has been found that the films have high sp^3/sp^2 ratio corresponding to good quality DLC thin films.

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