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Internal stresses and microstructures of commercial thick diamond films deposited by different deposition methods

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Abstract

Structures and stress state of six commercial freestanding thick diamond films (>300 μm) were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and Raman spectroscopy. These films represent the typical samples synthesized by three different chemical vapor deposition (CVD) methods, including DC arc, microwave plasma, and hot filament. It was found that the higher diamond deposition rate it reaches, the more non-diamond carbons it contains, and the larger the residual compressive stress it possesses. Moreover, the samples with the highest degree of optical transparency are under the lowest compressive stress. These crystal characteristics can be manipulated by selecting different deposition methods and parameters that affect nucleation rate and growth rate of diamond. The present results show that the DC arc method gives poorly developed crystals, and its residual compressive stress of the films is the highest due to the fastest diamond nucleation and crystal growth rates.

Keywords: Plasma-assisted CVD; Mechanical properties; X-ray diffraction; Optical properties

1. Introduction

Diamond has numerous unsurpassed properties, among them, bulk modulus, hardness, abrasion resistance and thermal conductivity are notable ones. The superb mechanical properties have made diamond the ideal abrasive for removing material from a workpiece. Hence, the industrial diamonds have been used conventionally to cut, grind, and polish ceramic and non-ferrous materials. The annual consumption of industrial diamond worldwide has reached about 250 t. However, a high-temperature and high-pressure process is generally used to synthesize all such diamonds. In the last decade, chemical vapor deposition (CVD) diamonds have emerged as the new premium cutting tools, and their worldwide sales are growing rapidly. There is an ever-increasing demand for using CVD diamonds to dissipate heat generated from high power electronic devices, such as laser diodes and microwave generators. Among various designs of CVD diamonds for these applications, the freestanding diamond films with a thickness more than 300 μm have been demonstrated to possess the highest performance.

Commercially, there are three CVD methods to produce commercial products: viz., DC arc, hot filament, and microwave plasma. All CVD methods are using atomic hydrogen to activate the formation of diamond. Therefore, the dissociation rate and efficiency of hydrogen molecules [1–6] can often control the optimal deposition rate. The DC arc can generate plasma with intense energy to produce a higher concentration of atomic hydrogen, hence, it can grow diamond film rapidly up to 100 $\mu m\,h^{-1}$ [1,2]. Both hot filament and microwave plasma are weaker in energy density in dissociating hydrogen molecules, so their growth rates are much lower, typically about 1 $\mu m\,h^{-1}$, but the growth can be accelerated to reach a rate of few $\mu m\,h^{-1}$ [3–6].

In this research, comparisons were made on diamond films synthesized by the typical three different CVD methods, viz., DC arc, hot filament, and microwave plasma. For applications in cutting tools and heat spreaders, the former demands a high impact resistance, so the diamond grains should be smaller with minimal internal stress. The latter requires a high thermal conductivity, so the diamond grains ought to be larger with minimal grain boundaries.

2. Experimental

The scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and Raman spectroscopy were used to characterize two samples each of CVD freestanding thick diamond films (>300 μm thick, >100 mm diameter) produced by DC arc, hot filament, and

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microwave plasma. These samples were obtained from commercial sources and were designated as D_c and D_p for samples produced by DC arc, as F_e and F_t for samples produced by hot filament, and as M_c and M_t for samples produced by microwave plasma, where c, p, e and t in the subscripts of each sample designation represent circular, polished, edge and translucent samples, respectively. The two translucent samples (F_t and M_t) are commonly referred to as thermal grade for making heat spreaders and the other four dark samples as tool grade for making cutting tools.

The morphology was examined by SEM and AFM. The roughness of the films was measured by Dektak 3030 profile meter. The crystal structure and lattice constants were determined by XRD. The polycrystalline Si powders of 325 mesh were spread on the surface of thick films as an internal standard to calibrate the XRD measurement. A least-squares refinement program LATT [7,8] was used to refine the lattice constants of the thick films. The Raman shift technique [9–19] was used to estimate the stress states near the surfaces of both sides of the thick films. The detailed procedures were described elsewhere [20]. Because of 1–2 μm diameter of the analysis spot in the present Raman spectrometer, the internal stress can be measured with a good lateral resolution. Based on the assumption that the distribution of diamond bands is Lorentzian and non-diamond bands, Gaussian, micro stress data were evaluated from spectra deconvolution that resolves the position and width for each peak.

3. Results and discussions

3.1. Film morphology

The SEM micrographs for the growth surface of the six commercial thick diamond films are shown in Fig. 1. It appears that the diamond crystals generated by microwave plasma (Fig. 1(a) and (b)) are relatively large (up to a size of 150 μm) and well developed. The crystals formed by hot filament (Fig. 1(c) and (d)) are about the same size but slightly inferior in crystal development. Diamond crystals synthesized under DC arc (Fig. 1(e) and (f)) appear to be finer with the least perfection in crystal development.

The translucent samples (F_t and M_t) do not show better-grown crystals. Thus, in contrast to single crystal diamond (e.g., gem diamond), the degree of optical transparency in these thick polycrystalline diamond films is not entirely determined by the degree of crystal perfection. As will be discussed later, it appears that the degree of transparency is sensitive to the presence of impurities and defects in the grains and grain boundaries. Hence, although the translucent samples and dark samples have similar morphology, the former ones appear to be less contaminated or to possess less defects than the latter. Because most impurities of dark samples are residual graphite and hydrogen with typical C=C and C–H chemical bond, they present strong absorbency ability in visible light. It is possible that microwave plasma has a better efficiency in dissociating hydrogen molecules to remove non-diamond impurities, and hence may produce diamond crystals with a higher degree of perfection. The hot filament method, being a lower energy process, could have a slower kinetics to remove non-diamond impurities, such as graphite, hence, the crystals may contain slightly more impurities and defects. Although hot filament method may not concentrate the energy as much as microwave plasma, it can spread out the heating area and hence expand the growth zone. Thus, hot filament method has demonstrated the ability to deposit the largest area of diamond film with the smallest electric power. In our experience, a 35 kW hot filament reactor in our laboratories can coat diamond in an area as large as $30 \times 30\,cm^2$. For a microwave system to cover the same area, more than twice the power may be needed.

According to Fig. 1, the diamond films produced by DC arc method appear to be the least perfect, and their diamond crystals are much finer (less than 30 μm in size) on the growth side surface. A DC arc could reach a much higher temperature (about 6000°C) than that of microwave plasma and hot filament. As a result, the dissociation of atomic hydrogen would be most complete. Although the presence of a higher concentration of atomic hydrogen can help the diamond growth, the rapid growth rate fueled by the high speed jet of reactive gases tends to rush the growth, and power densities of DC arc are too high and difficult to control the substrate temperatures near a range 1100–1150°C, which makes the crystals imperfect.

Fig. 2 shows the AFM micrographs for the sides that are in contact with the substrate (typically made of molybdenum), i.e., micrographs on nucleation side of the thick films. It appeals that nucleation density of DC arc method is higher than the other two methods due to action of dense plasma from intense energy input and material flux in DC arc method. As a result, crystal imperfections are abundant in the grown film. Table 1 shows that the roughness, R_a, of all six thick film samples is ranging from 301.1 to 624.1 nm on the nucleation side, and from 3230.0 to 19,729.0 nm on the growth side. In other words, growth competition among neighbor crystals results in a great difference in roughness on nucleation and growth sides.

3.2. Bonding and stress states

Figs. 3 and 4 show the Raman spectra of the six thick films for growth and nucleation sides, respectively. It depicts that the diamond (sp^3) bonds are better developed on the growth surface than on the nucleation surface. Moreover, these spectra reveal that the sample D_c contains the highest amount of graphitic bonds (sp^2) of carbon. The large amount of graphitic bonds could have impaired the free growth of diamond crystals, and hence hindered the development of perfect facets (Fig. 1(e) and (f)). Again, the Raman spectra also imply that the high growth rate of DC arc method could have resulted in larger amount of graphitic bonds, and insufficient development of crystal shape.

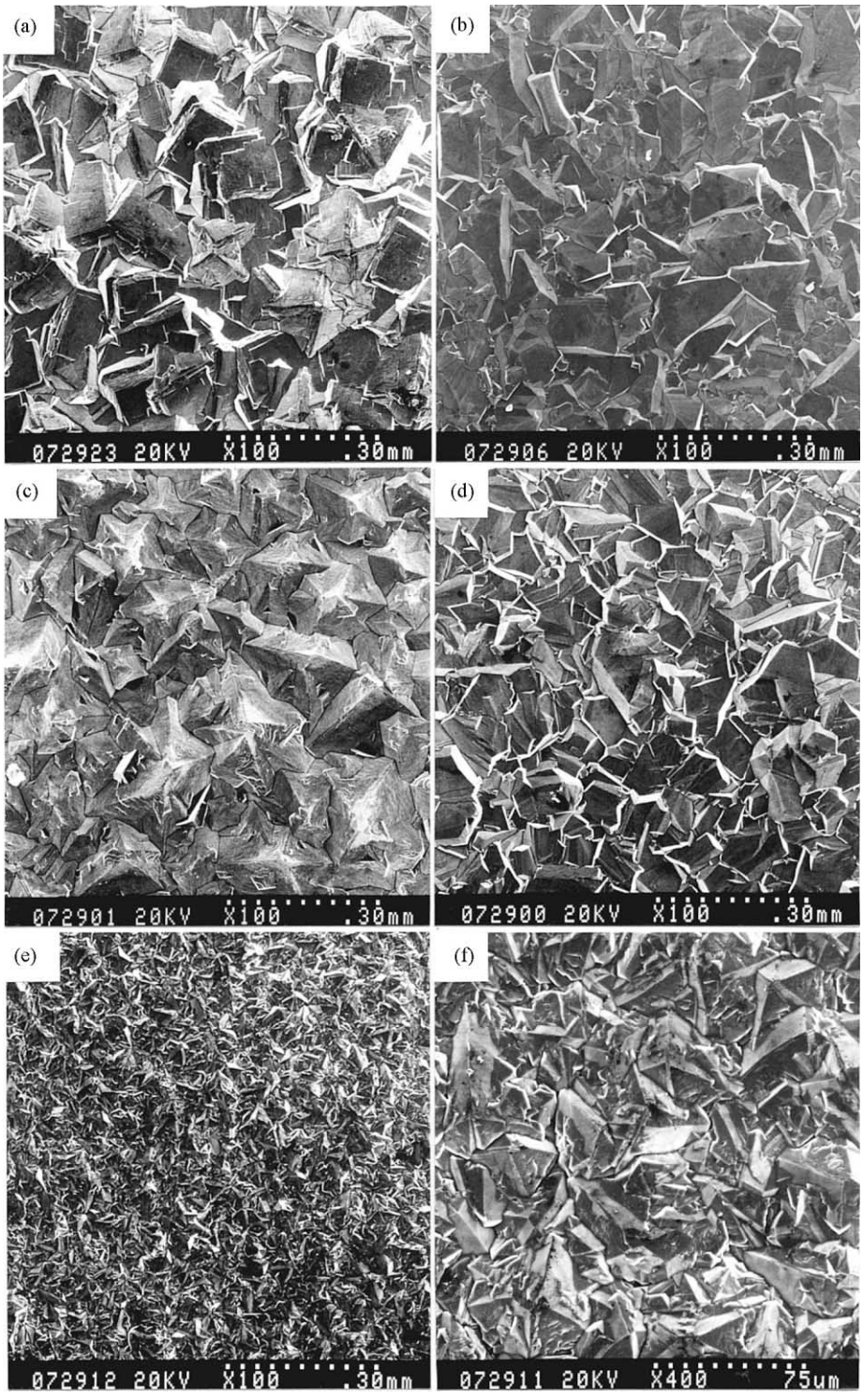

Fig. 1. The SEM morphologies on the growth sides of the thick diamond films: samples (a) M_c, (b) M_t, (c) F_e, (d) F_t, (e) D_c, (f) D_c.

Based on the Raman peak shift for both sides of these diamond films, the states of residue stress are calculated and listed in Table 1. In the case of freestanding films, the stress induced by thermal stress and the epitaxial attachment to the substrate will be relieved, so the measured residual stress is essentially the intrinsic stress of the films. As reported, the intrinsic stress in the films is mainly from the effect of the non-diamond carbon content in the diamond crystals, not in the crystal boundaries [20]. A higher non-diamond carbon content in the films will generally result in a greater compressive stress in the film owing to its large specific volume (1.5 times that of diamond) [20,21]. Table 1 indicates that

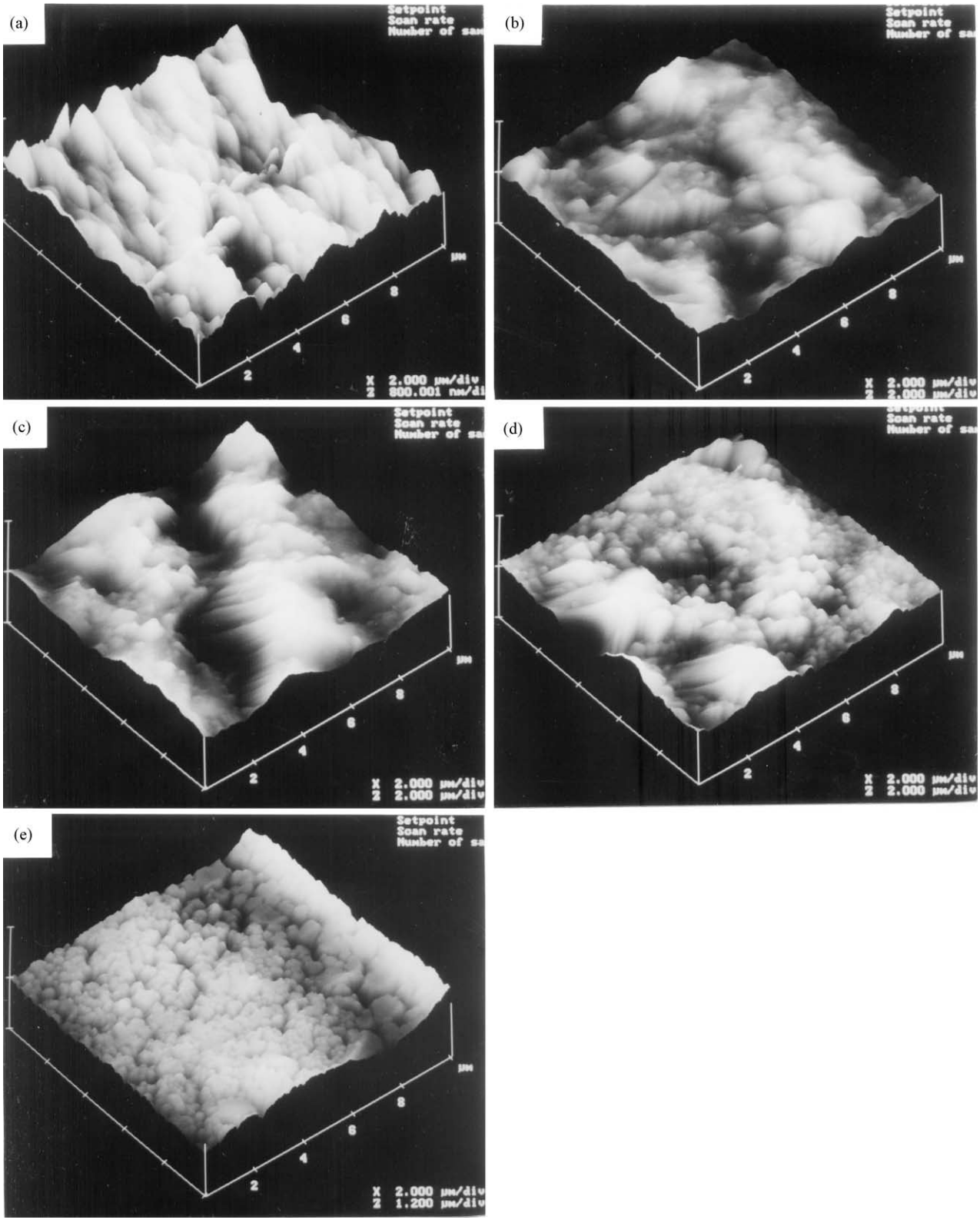

Fig. 2. The AFM morphologies on the nucleation sides of the thick diamond films: samples (a) M_c, (b) M_t, (c) F_e, (d) F_t, (e) D_c.

Table 1
Structures and internal stress of six commercial freestanding thick diamond films deposited by DC arc, microwave plasma CVD and hot filament methods

	Microwave plasma		Hot filament		DC plasma jet	
	M_c	M_t	F_e	F_t	D_c	D_p
R_a on nucleation surface (nm)	301.1	624.1	529.7	435.2	456.0	
R_a on growth surface (nm)	9931.0	4164.0	19729.0	4985.0	3230.0	
Non-diamond content near nucleation surface (%)	0.95	0.73	1.17	0.71	1.27	
Non-diamond content near growth surface (%)	0.49	0.46	N/A	0.22	1.24	1.19
Stress near nucleation surface (GPa)	−9.53	−6.36	−6.84	−5.41	−11.59	−10.0
Stress near growth surface (GPa)	−0.86	−0.49	−0.61	−0.48	−1.56	−1.01
I/I_0, d (Å) for (1 1 1)	1000, 3.570	154, 3.582	12, 3.539	1000, 3.570	340, 3.611	155, 3.562
I/I_0, d (Å) for (2 2 0)	699, 3.569	1000, 3.572	1000, 3.542	729, 3.570	1000, 3.546	1000, 3.575
I/I_0, d (Å) for (3 1 1)				318, 3.570		
I/I_0, d (Å) for (4 0 0)				16, 3.569		
I/I_0, d (Å) for (3 3 1)				625, 3.567		
Average lattice constant a (Å)	3.567	3.569	3.562	3.569	3.544	3.566

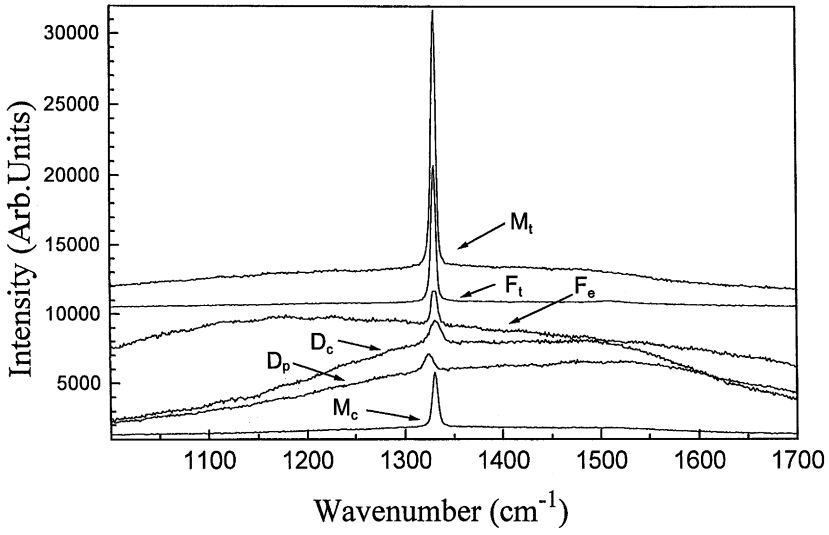

Fig. 3. The Raman spectra on the growth sides of the thick diamond films.

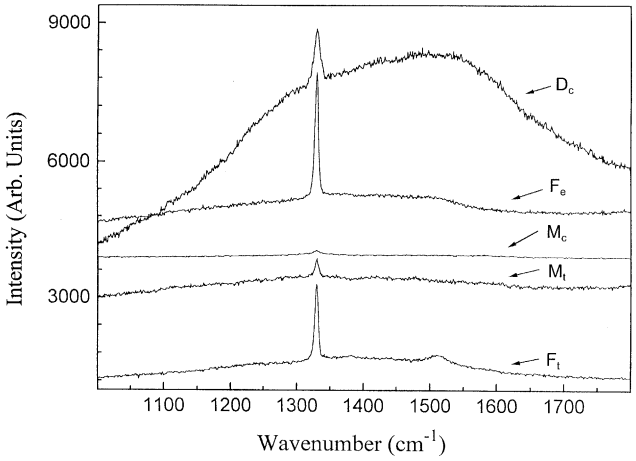

Fig. 4. The Raman spectra on the nucleation sides of the thick diamond films.

all samples are under large compressive stress. Moreover, the compressive stress on the growth surface is an order of magnitude lower than that on the nucleation surface. For the same reason, the compressive stress is significantly lower for the translucent samples than for the dark samples due to a lower non-diamond carbon content in the translucent samples. In other words, a higher growth rate could lead to a higher concentration of non-diamond carbon in both diamond crystals and crystal boundaries, and result in a greater compressive stress.

From the above analyses, the compressive stress in the diamond films synthesized by DC arc method is the highest, and then the films deposited by microwave plasma are the next. The compressive stress is the least for diamond films formed by hot filament method. This trend is parallel with the decreasing growth rate of diamond. Thus, the higher diamond deposition rate it reaches, the more non-diamond carbon it contains, and the larger compression the crystal

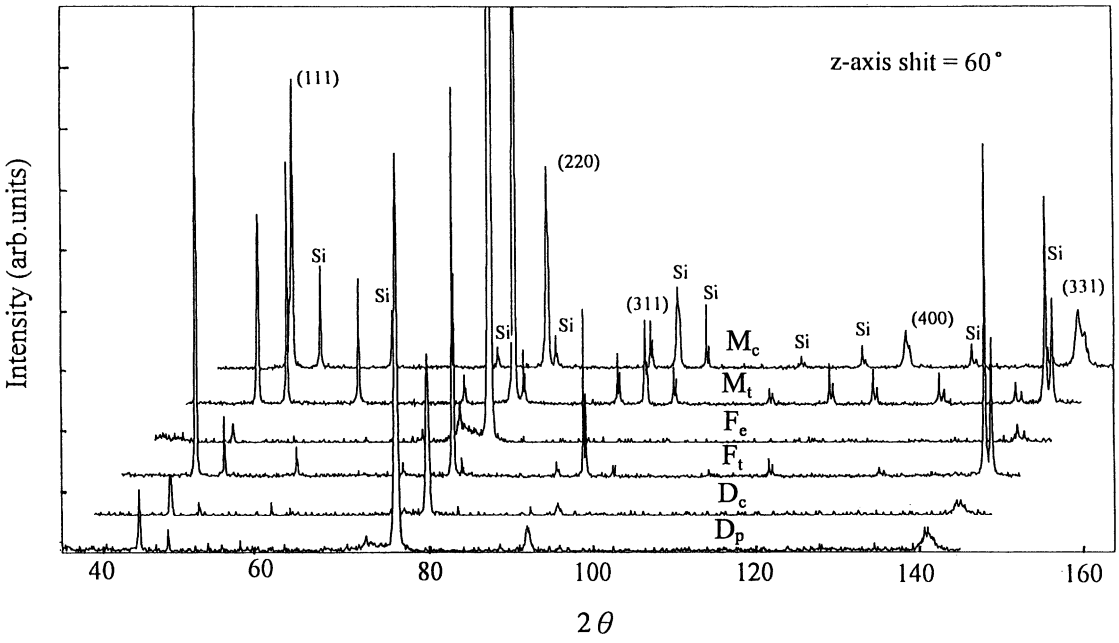

Fig. 5. The XRD patterns on the growth sides of the thick diamond films.

receives. The DC arc process, being the fastest growth process for commercial diamond films, could produce diamond films with the least amount of diamond content and under the highest magnitude of compressive stress.

The nucleation sides of the two diamond films produced by DC arc are under a compressive stress of about 10 GPa, which is more than 2% of the bulk modulus (443 GPa) of gem diamond. This compressive stress is nearly twice the high-pressure used for commercial synthesis of diamond. Such a high stress could contract the volume of diamond by more than 1%, and reduce the size of diamond by more than 0.3%.

3.3. Crystal structure and lattice parameters

Fig. 5 shows XRD profiles of these six samples, and the indexing of major peaks of diamond. Based on the positions of these peaks, lattice parameters of diamond are calculated along with *d*-spacings of common planes. These *d*-spacings are compared with stress-free diamond. The amount of *d*-spacing reductions are tabulated and listed along with the above stresses calculated based on Raman data, as shown in Table 1. The comparison of *d*-spacings and compressive stresses reveals that the shrinking of the former correlated well with the magnitude of the latter for diamond films deposited by the same method. Moreover, the highest amount of shrinkage is consistent with that predicted from the compressive stress. It is noted that the wider separated planes, e.g. (1 1 1), moved closer to each other by compression because they are set farther apart to begin with. Hence, the reduction of *d*-spacings is not uniform throughout the lattice, but the strain of each plane is about the same.

Table 1 also reveals that the translucent diamond films contain the least compressive stress or least amount of non-diamond carbons, which are the materials to absorb and scatter the incident light, and to degrade the transparency of the films. Hence, the ways to eliminate the compressive stress are important for making the diamond film more transparent.

4. Conclusions

The unique characteristics of the commercial products of freestanding thick diamond films deposited by different CVD techniques were examined. The DC arc method possesses the fastest diamond nucleation and crystal growth rates. The higher deposition rate tends to form smaller and poorly developed crystals. These tiny imperfect crystals could trap more non-diamond carbons in diamond crystals. As a result, the faster deposited diamond films are more highly compressed with stress in the crystal lattice. On the other hand, the hot filament and microwave plasma methods could deposit larger diamond crystals with less residual compressive stress and more transparency. In other words, the ways to make the diamond thick films more transparent are to reduce the non-diamond carbon content or compressive stress in the films.

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