Origins of the residual stress in CVD diamond films

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Abstract

Diamond films were deposited on (100) Si wafer, WC (5%Co) and quartz substrate materials by a microwave plasma chemical vapor deposition (CVD) system. The effects of deposition and substrate conditions on residual stress of the films were systematically investigated. The films were characterized by scanning electron microscopy, X-ray diffraction, Raman and indentation adhesion testing. The film structure including its non-diamond carbon content, crystal size, texture coefficient, film thickness and surface roughness were examined. The results show that the residual stress of the films is a function of the surface pretreatment, in addition to the substrate material and deposition conditions. The origins of the residual stress are mainly the thermal stress and the intrinsic stress. The intrinsic stress is mainly from the effect of the non-diamond carbon content in the diamond crystals, not at the crystal boundaries. A greater non-diamond carbon content in diamond crystals results in a greater residual stress. The texture of the films has no significant effect on the residual stress. A low compressive residual stress on Si wafer is beneficial to the adhesion of the film.

Keywords: Diamond film; Residual stress; Interface structure

1. Introduction

It is well known that diamond is a unique material in both fundamental science and engineering applications. Therefore, the growth of chemical vapor deposition (CVD) diamond films on various substrates has been the subject of expanding interest. One of the major issues of concern for CVD diamond films is to understand the origins of the residual stress of the films, so that we can manage and control these stresses. In general, the possible origins of the residual stress include thermal stress, phase transformation stress, epitaxial stress, and intrinsic stress, etc. Thermal stress is formed during the cooling down stage after the deposition, and is due to the difference in thermal expansion coefficient between the film and the substrate. Stress can also be induced due to phase transformations of the films or substrate during cooling from the deposition temperature to the lower temperatures. For a substrate and film with similar crystal structure but different lattice constants, the interface structure between the film and the substrate can be semicoherent or coherent. The stress so developed is called "epitaxial stress". The stress can also formed due to the presence of defects, such as grain boundaries, dislocations, voids and impurities, etc., and this stress is called "intrinsic stress". There are many techniques used to analyze residual stresses in the films. Raman spec-

troscopy is one of the methods used by many authors to assess the residual stress in the diamond films [1-8], and is also one of the most important tools for characterizing CVD diamond. In the present report, Raman spectroscopy was used to analyze the stresses in the diamond films. The origins of the residual stress in diamond films are discussed.

2. Experimental details

Diamond films were deposited on (100) Si wafer, quartz and cemented 5% Co–WC substrates by a microwave plasma CVD system with CH_4 and H_2 as the source gases. The surface morphologies of the films and substrates were examined by scanning electron microscopy (SEM). The substrates were subjected to a few different surface pretreatments to obtain different surface roughness values from $1 \sim 50$ nm, including polishing with 0.1, 1.0 and 6 μm diamond paste, 30 μm diamond-coated sheet, and 1 μm polishing cloth. The deposition conditions were: $0.4/100 \sim 1/100$, CH_4/H_2 ratio; $973 \sim 1173$ K; $200 \sim 480$ W, microwave power; $15 \sim 35$ Torr, total pressure; $0.2 \sim 17$ h.

X-ray diffraction (XRD) analysis was performed on the films. The texture coefficient, $T(hkl)$, for each (hkl) reflection was calculated from

$$T_{(hkl)} = [I_{(hkl)}/I_{0\,(hkl)}]/\{(1/4)\Sigma[I_{(hkl)}/I_{0\,(hkl)}]\} \qquad (1)$$

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where $I_{(hkl)}$ is the relative intensity of the (hkl) plane of the diamond film, and $I_{0\ (hkl)}$ is the relative intensity of the (hkl) plane of a randomly oriented polycrystalline film, and is assumed to be the same as the JCPDS powder diffraction files. $T_{(hkl)}$ represents a measure of the growth randomness or preferred orientation. For a randomly oriented polycrystalline film, the theoretical value is 1.0.

The adhesion of the films was determined by the indentation adhesion testing method, which was described in detail elsewhere [9]. The diameter of the cracked area, X, versus the indentation load, P, was recorded. The slope of the curve, dX/dP, is used as a measure of the quality of adherence between the film and the substrate. A greater value indicates a poorer adherence.

The film quality, non-diamond carbon content and residual stresses of the films were assessed by the Raman spectroscopy. Raman spectroscopy was developed by LeGrice et al. [4] to analyze the stress in diamond films. Although the beam area of Raman spectroscope is about 10 μm in diameter, which is much greater than the grain size of the films in the present conditions, it is realized that the Raman spectroscopy measures the relatively localized stresses by comparing with the X-ray and substrate curvature methods. It is found that both the stress and the microcrystalline domain size can contribute to a frequency shift of Raman peak. The peak will shift to lower frequency as the crystalline domain size decreases, but also the full width at half-maximum (FWHM) increases. In general, a material which is under tensile strain will exhibit a Raman peak which is shifted to lower frequency, while the Raman peak of a material undergoing a compressive strain is shifted to higher frequency. Therefore, the total observed shift of the peak, $\Delta\omega_{ob}$, can be expressed by

$$\Delta\omega_{ob} = \Delta\omega_d + \Delta\omega_s \qquad (2)$$

where $\Delta\omega_d$ is the shift due to domain size effect, and $\Delta\omega_s$ is the shift due to stress. According to Van Acker et al. [5], the Raman peak shift of the film under stress, $\Delta\omega_s$, is given by

$$\Delta\omega_s = -P\sigma \qquad (3)$$

where σ is the in-plane balanced biaxial stress, and P is a function of Grueneisen parameter, Poisson ratio and bulk modulus of the film. The value of P for diamond films was evaluated by many authors to be $1.70 \sim 3.05$ cm^{-1} GPa^{-1} [4–7]. In the present report, $P = 2.23$ cm^{-1} GPa^{-1} was used to estimate the internal stress of diamond films. By considering the sensitivity of Raman signal for non-diamond carbon phase is about 75 times of that for diamond, Raman spectroscopy was also used to estimate the non-diamond carbon content, C_{nd}, in the film by the relation [8]

$$C_{nd} \approx 1/[1 + 75(I_d/I_{nd})] \qquad (4)$$

where I_d is Raman peak intensity for diamond crystals, and I_{nd} is the Raman peak intensity for a non-diamond carbon phase.

3. Results and discussion

3.1. Film morphology and quality

The SEM morphologies of diamond films revealed that they depend upon the deposition conditions, substrate pretreatments and substrate materials. Fig. 1 shows some typical film morphologies under various conditions for different substrate materials (WC (5%Co), quartz and (100) Si wafer). The films are smooth, small grained, and polycrystalline. Raman spectroscopy revealed that the films contain diamond and non-diamond carbon phases, as evidenced by a narrow peak around 1332.5 cm^{-1} and a broad peak around 1560 cm^{-1}. Fig. 2 presents the typical Raman spectra for three different substrate materials. The spectra under various conditions all showed the characteristic diamond peak. The non-diamond carbon content of diamond films was determined by Eq. (4). Fig. 3 shows effects of deposition time, substrate pretreatments and materials on non-diamond carbon content of the films.

3.2. Effect of non-diamond carbon content on residual stress

The magnitude of the Raman shift from the peak position of 1332.5 cm^{-1} for natural diamond, $\Delta\omega_{ob}$, and the FWHM of the diamond film peak were measured. Based on the relation between $\Delta\omega_d$ and FWHM, as determined by LeGrice et al. [4], the magnitude of the shift due to domain size effect can be estimated by measuring the FWHM. The shift due to stress alone can then be determined from Eq. (2). For Si wafer substrates, the residual stress of diamond crystals, which has not yet formed a film, is from -2.55 to -0.42 GPa. The deposition conditions for these two boundary cases are 1173 K, 1 h, 35 Torr, 480 W, 16 nm roughness, 1% methane, and 1173 K, 0.2 h, 35 Torr, 480 W, 8 nm roughness, respectively. The negative sign indicates a compressive stress. Similarly, the residual stress of diamond crystals is from -2.53 to -0.84 GPa, and from -1.01 to 0.23 GPa for WC and quartz substrate materials, respectively. It implies that the residual stress is not related to the non-diamond carbon phase at the grain boundaries. In terms of the grain boundary relaxation model, it was proposed by Windischmann et al. [10] that the tensile intrinsic stress is related to a voided microstructure at the grain boundaries. The comparable strong compressive residual stresses for both diamond crystals and diamond films reveal that the contribution of grain boundary relaxation is small in the present conditions.

For Si wafer substrate materials, the residual stress of diamond films is from -2.42 to -0.08 GPa. Fig. 4 shows the effect of deposition time on the internal stress of diamond films on three different substrates. Curve b in Fig. 4 is for the films on Si wafers. The deposition temperature in this case is 1173 K. Therefore, the thermal stress is about -1.68 GPa ($\approx 1200 \times (2.6-1) \times 10^{-6} \times (1173-298)$), and the epitaxial stress is about 17 GPa (assuming coherent boundary to match three carbon atoms with two Si atoms) [11]. There is no phase transformation between the deposition tempera-
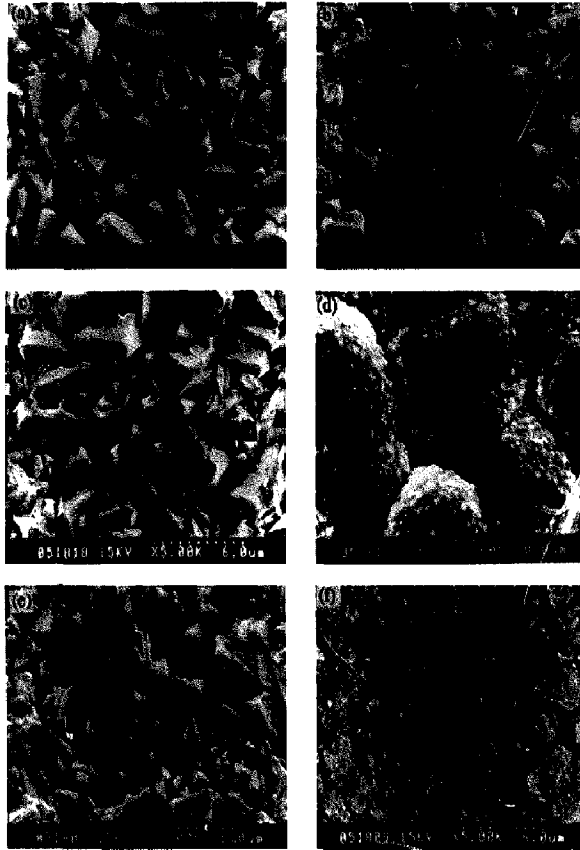
Fig. 1. Typical diamond film morphologies on different substrates and at different deposition conditions: (a) on a Si wafer, 10 h, 1173 K; (b) on a Si wafer, 5 h, 973 K; (c) and (d) on WC (5%Co), 1173 K, 1 nm and 20 nm roughness; (e) and (f) on quartz, 1073 K and 973 K.

ture and room temperature for both the substrate and film. In other words, the epitaxial stress and phase transformation stress should not be the main contributions, and the thermal stress and intrinsic stress may be the main factors. It is noteworthy that curve b in Fig. 4 is comparable with curve d in Fig. 3 for non-diamond carbon content in the films. By assuming Young's modulus of graphite is 10 GPa and the volume expansion from amorphous carbon (density, 3 g cm^{-3}) to graphite (density, 2.4 g cm^{-3}), the corresponding compressive stress is about -0.8 GPa ($= 10 \times [(1/3)^{1/3} - (1/2.4)^{1/3}]/[(1/3)^{1/3}]$). Therefore, the intrinsic stress due to transformation of non-diamond carbon to the more stable graphite in the films may be one of the important factors to the residual stress of diamond films. A greater non-diamond carbon content in the films gives rise to a greater compressive stress. A similar relation is also seen by comparing both curve c in Fig. 4 and Fig. 3 for the films on WC substrate. Curves b and c in Fig. 5 reveal that a greater methane con-

centration in the source gases results in a greater compressive stress in the film due to a higher non-diamond carbon content in the film. This point is in agreement with the conclusions of Windischmann et al. [10].

For the WC substrate material, curve c in Fig. 4 shows the effect of deposition time on the stress of the films. The thermal stress in this case is about -3.99 GPa [12], and the intrinsic stress due to presence of non-diamond carbon is also compressive in nature. Therefore, the residual stresses of the films on both WC and Si wafer are all compressive in nature.

For quartz substrate material, the thermal stress for a deposition temperature of 1173 K is about 0.47 GPa [13], and it is a tensile stress. Therefore, as shown in curve a of Figs. 4 and 5, the residual stress can be either compressive or tensile, depending upon the sum of tensile thermal stress and compressive intrinsic stress, which is due to the presence of non-diamond carbon in the films.
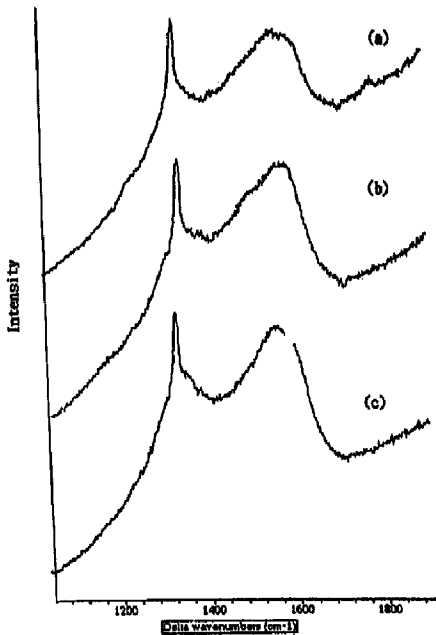
Fig. 2. The typical Raman spectra of diamond films on three different substrate materials: (a) Si substrate, 1173 K, 8 nm roughness; (b) WC substrate, 1173 K, 1 nm roughness; (c) quartz substrate, 973 K, 8 nm roughness.
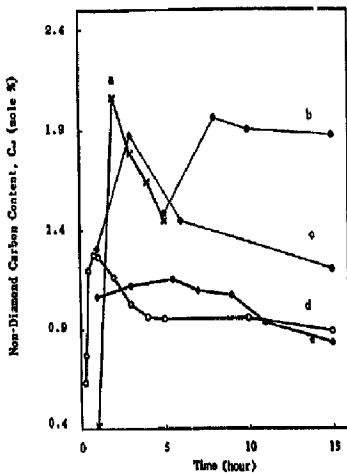

Fig. 3. Effects of deposition time, substrate pretreatments and materials on the non-diamond carbon content of the films: curve a, quartz, 973 K, 8 nm roughness; curve b, WC, 1173 K, 20 nm roughness; curve c, WC, 1173 K, 1 nm roughness; curve d, Si, 1173 K, 8 nm roughness; curve e, Si, 1173 K, 16 nm roughness.
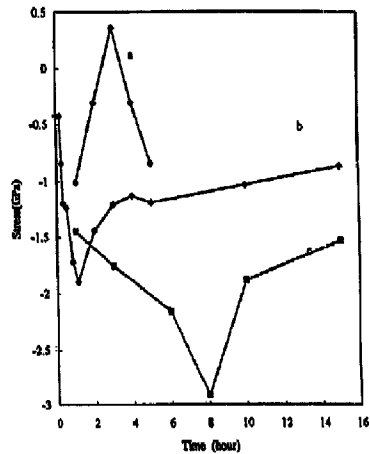

Fig. 4. Effect of deposition time on the internal stress of diamond films on three different substrates: curve a, films on quartz, 973 K; curve b, films on Si wafers, 1173 K; curve c, films on WC (5%Co), 1173 K.
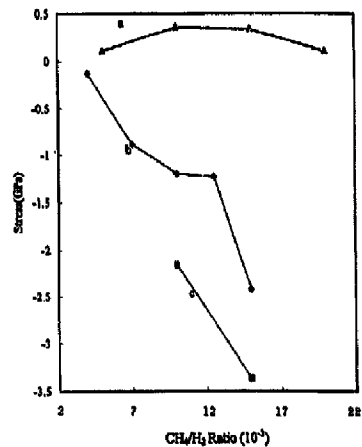

Fig. 5. Effect of CH_4/H_2 ratio on the internal stress of diamond films on three different substrates: curve a, films on quartz, 973 K, 2.5 hr; curve b, films on Si wafers, 1173 K, 3 hr; curve c, films on WC (5%Co), 1173 K, 5 h.

The effect of surface roughness of the WC substrate on residual stress of the films is shown in Fig. 6. A rougher surface, e.g. curve b in Fig. 6, gives a greater compressive stress in the film due to a greater non-diamond carbon content in the films. The effect of surface roughness on adhesion of the film was investigated by our group [14]. It was concluded that there exists an appropriate range of the substrate roughness values for an optimum adhesion strength. This is related to a greater nucleation density of diamond crystals and a lower non-diamond carbon content in the film in certain roughness range.
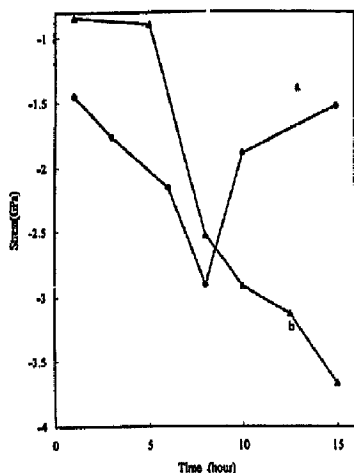
Fig. 6. Effects of deposition time and surface roughness of the substrate on the internal stress of diamond films on WC (5%Co) substrates: curve a, roughness = 1 nm; curve b, roughness = 20 nm.

3.3. Effect of the film thickness and texture coefficient on residual stress

Fig. 7 shows effect of the film thickness on residual stress of the films on three different substrate materials. For a thickness greater than 8 μm, it revealed that a greater thickness results in a less compressive stress in the film. This may related to a lower non-diamond carbon content near surface of the thicker film, and to the fact that the penetration depth of the laser beam for generating the Raman signals is so limited. Therefore, for a thicker film the Raman shift may nor respond the stress state of the entire film.

Fig. 8 shows effect of texture coefficient on residual stress of the films on WC and Si wafer substrates. It indicates that the texture of the film is not a significant factor on the residual stress.

3.4. Effect of residual stress on adhesion of the film

It is interesting to know how the residual stress affects the adhesion of the films. In many engineering applications, a
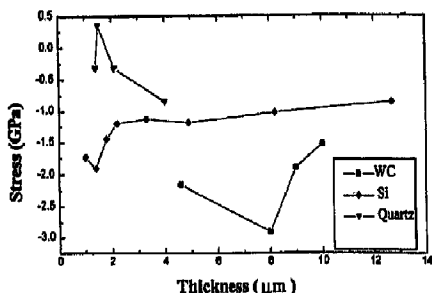

Fig. 7. Effect of the film thickness on residual stress of the films on WC, quartz and Si substrate materials.
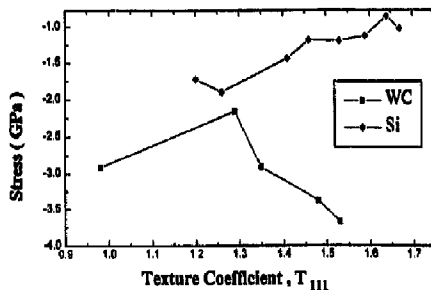

Fig. 8. Effect of the texture coefficient on residual stress of the films on WC and Si substrate materials.
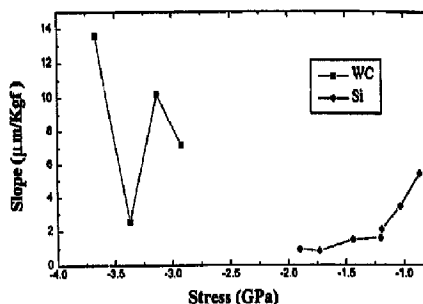

Fig. 9. Effect of the residual stress on adhesion of the diamond films on WC and Si substrate materials.

compressive stress is often intentionally applied to the surface of a component to increase its cracking resistance. Fig. 9 shows residual stress versus slope, where the slope is a measure of the crack propagation ability of the film, i.e. the slope of the cracking diameter versus indentation load curve. A greater slope indicates a smaller cracking resistance or adhesion. At lower compressive stresses, a greater compressive stress seems to result in a favorable cracking resistance. At higher compressive stresses, there is not enough data to make a definitive statement.

4. Conclusions

The residual stress of CVD diamond films on three different substrate materials were determined by micro-Raman spectroscopy. The X-ray diffraction was used to determine the texture coefficient of the films, and the indentation testing method was used to evaluate the cracking resistance of the film on the substrate. It is found that the residual stress of the films on (100) Si wafer and WC materials is compressive in nature, and is both compressive and tensile in nature for quartz substrates. The origins of the residual stress are mainly the sum of thermal stress and intrinsic stress. The thermal stresses for WC and Si wafer substrates are compressive, whereas those for quartz substrates are tensile. The intrinsic stress arises mainly from the effect of non-diamond carbon

content in the diamond crystals, not at the grain boundaries. A greater non-diamond content in the diamond crystals will result in a larger compressive residual stress. It is also found that the texture of the films has no significant effect on the residual stress. For a high cracking resistance of the films on Si substrates, a smaller compressive stress is necessary.

Acknowledgements

References

[1] J.A. Baglio, B.C. Farnsworth, S. Hankin, G. Hamill and D. O'Neil, Thin Solid Films, 212 (1992) 180.

[2] Wang Wanlu, Liao Kejun, Gao Jinying and Liu Aimin, Thin Solid Films, 215 (1992) 174.

[3] P.K. Bachmann, H.D. Bausen, H. Lade, D. Leers, D.U. Wiechert, N. Herres, R. Kohl and P. Koidl, Diamond Related Mater., 3 (1994) 1308.

[4] Y.M. LeGrice, R.J. Nemanich, J.T. Glass, Y.H. Lee, R.A. Rudder and R.J. Markunas, Mater. Res. Soc. Symp. Proc., 162 (1990) 219.

[5] K. Van Acker, H. Mohrbacher, B. Blanpain, P. Van Houtte and J.P. Celis, Mater. Res. Soc. Symp. Proc., 308 (1993) 677.

[6] C. Johnson, A. Crossley, P.R. Chalker and I.M. Buckley-Golder, Diamond Related Mater., 1 (1992) 450.

[7] H. Boppart, J. van Straaten and I.F. Silvera, Phys. Rev. B, 32 (1985) 1423.

[8] M. Silveira, M. Becucci, E. Castellucci, F.P. Mattiot, V. Barbarossa, R. Tomaciello and F. Galluzzi, Diamond Related Mater., 2 (1993) 1257.

[9] C.T. Kuo, T.Y. Yen and T.H. Huang, J. Mater. Res., 5 (1990) 2515.

[10] H. Windischmann, G.F. Epps, Y. Cong and R.W. Collins, J. Appl. Phys., 69 (1991) 2231.

[11] M. Alam, D.E. Peebles and J.A. Ohlhausen, J. Adhesion Sci. Technol., 7 (1993) 1309.

[12] M. Nesladek, Diamond Related Mater., 2 (1993) 98.

[13] K. Fabisiak, J.M. Philippoz and H. van der Berg, Diamond Related Mater., 1 (1992) 77.

[14] T.H. Huang, C.T. Kuo and T.S. Lin, Scr. Metall., 26 (1992) 1481.