Nondestructive characterization of the film quality and stress states in diamond films on various substrates

Cheng-Tzu Kuo, Jin-Yu Wu and Shien-Lien Chou

Department of Materials Science and Engineering, National Chiao Tung University
1001 Ta-Hsueh Road, Hsinchu 300 Taiwan
ctkuo@cc.nctu.edu.tw

ABSTRACT

Diamond films deposited on various substrates were characterized nondestructively by Raman spectroscopy and X-ray diffraction (XRD) to evaluate their stress states and film quality. The X-ray diffraction method is further divided into two methods, i.e., the low incident beam angle X-ray diffraction (LIBAD), and Clemens-Bain method for the textured films. The whole-pattern-fitting structure refinement method, or called "Rietveld method" was adapted in XRD method to improve its accuracy. The film adhesion, film morphology and film structures including its non-diamond carbon content, crystal size, texture coefficient, film thickness and surface roughness were also examined. The correlations between structure and residual stress of the films on various substrates and under various deposition and pretreatment conditions were analyzed. The feasibility of nondestructive evaluation the film quality and stress states, and the origins of the residual stress of the films were discussed.

Keywords: Nondestructive testing, diamond films, Raman spectroscopy, X-ray diffraction, Rietvelt analysis, residual stress, textured films.

1. INTRODUCTION

One of the major issues of concern of a protective coating is that coatings must possess adequate adhesion to the substrate. In this regard, the presence of residual stress is an important aspect of film reliability, and to characterize nondestructively the film quality and stress state is often the most desired technology in engineering applications. In general, the possible sources of the residual stress include thermal stress, phase transformation stress, epitaxial stress and intrinsic stress. Thermal and phase transformation stresses are formed during the cooling down stage after deposition. The former one is due to the difference in thermal expansion coefficient between the film and the substrate. The latter one is induced due to phase transformations of the film and/or the substrate. For a substrate and a 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 be formed due to presence of defects, such as grain boundaries, dislocations, voids and impurities, etc., and is called "intrinsic stress".

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2. EXPERIMENTAIL DETAILS

The X-ray diffraction (XRD) and Raman spectroscopy are two important nondestructive methods used by many researchers to assess the residual stress[1-8]. The XRD method is further divided into two methods, i.e. the low incident beam angle X-ray diffraction (LIBAD)[1], and Clemens-Bain method developed for the textured films[2]. The whole-pattern-fitting structure refinement method, or called "Rietveld method" was adapted in LIBAD and Clemens-Bain method to improve its accuracy. For diamond films, the diffraction peak of (311) plane was used in LIBAD method to increase its accuracy. The stress equation for the (111) textured films was adapted to calculate the residual stress in Clemens-Bain method. By assuming equal biaxial stress in the films with cubic crystal structure, the strain at angle ψ with the perpendicular line of the (111) textured film surface, ε_ψ , can be expressed by[2]:

$$\varepsilon_\psi = \frac{(d_\varphi - d_o)}{d_o} = \sigma(\frac{2S_{11} + 4S_{12} - S_{44}}{3} + \frac{S_{44}}{2}\sin^2\varphi)$$

where d_ψ and d_o are interplane spacing, and S_{11}, S_{12}, S_{44} are X-ray elastic compliance which can be determined from X-ray elastic constants. The X-ray stiffness constants for diamond crystal were assumed[9] : C_{11} = 1078 GPa, C_{12} = 125 GPa and C_{44} = 577 GPa.

In Raman spectroscopy, it is found that both stress and the micro-crystalline domain size can contribute to a frequency shift of Raman peak[3-7]. The peak will shift to lower frequency as the crystalline domain size decreases, but the full width at half maximum increases. In general, a material under tensile strain will result in a shift of Raman peak to lower frequency. Therefore, the total observed shift of a Raman peak, $\Delta\omega_{ob}$, can be expressed by: $\Delta\omega_{ob} = \Delta\omega_d + \Delta\omega_s$, where $\Delta\omega_d$ is the shift due to domain size effect, and $\Delta\omega_s$ is the shift due to stress effect. According to Acker et al.[6], the Raman peak shift of the film under stress, is given by: $\Delta\omega_s = -P\sigma$, where σ is the in-plane balanced biaxial stress, and P is a function of Grueneisen parameter, Poisson's ratio and bulk modulus of the film. The value of P for diamond films was evaluated by many authors[3-7] to be 1.70 ~ 3.05 $cm^{-1}GPa^{-1}$. In the present report, P = 2.23 $cm^{-1}GPa^{-1}$ was used. The Raman spectroscopy is also the tool for characterizing the film quality, i.e. non-diamond carbon content. By considering the sensitivity of Raman signal for non-diamond carbon phases is about 75 times of that for diamond, the non-diamond carbon content, C_{nd} , in the film can be expressed by the relation[4]: $C_{nd} = [\ 1 + 75(\ I_d/I_{nd}\ )\ ]^{-1}$, where I_d and I_{nd} are Raman peak intensities for diamond crystals and non-diamond carbon phases, respectively. The detailed procedures of Raman stress analyses were described elsewhere[8].

With CH_4 and H_2 as the source gases, diamond films were deposited on (100) Si wafer by both microwave plasma chemical vapor deposition method (MPCVD) and hot filament method, and on quartz and cemented carbides (5% Co+WC) by MPCVD. The results for the films deposited on Si wafer, quartz and cemented carbides by MPCVD were described elsewhere[8].

3. RESULTS AND DISCUSSION

3.1 Effect of film quality on residual stress

From the results of Kuo's group[8], it indicates that the residual stress of the films on Si wafer and cemented carbide substrates is compressive in nature. And is both compressive and tensile in nature for quartz substrates. The origins of the residual stress in diamond films are mainly the sum of thermal stress and intrinsic stress. The intrinsic stress is compressive in nature and arises mainly from the effect of non-diamond carbon content in the diamond crystals, not at the grain boundaries. A greater non-diamond carbon content will result in a larger compressive stress. Figure 1 shows effect of methane concentration of the source gases on residual stress, which was determined by Clemens-Bain method. A higher methane concentration results in a greater non-diamond carbon content in diamond crystals, and results in a greater compressive stress, as shown in Fig. 1 by the curve for 10 hr deposition time. For thicker films, effect of methane concentration is not obvious, as revealed in Fig. 1 by the curves for 15 and 20 hr deposition times. This is due to the fact that the penetration depth of X-ray is limited , and the stress value so evaluated may merely represent the stress near the surface side of the films.

3.2 Comparison of different stress-evaluation methods

For comparison among three different analysis methods, i.e., LIBAD, Clemens-Bain method and Raman method, the residual stresses in diamond films on Si wafer deposited by hot filament method under different deposition conditions are shown in Table 1. The negative value indicates a compressive stress. Each stress in Table 1 is an average value of three measurements. The stress ranges analyzed by LIBAD, Clemens-Bain and Raman method are –0.750 ~ -4.243, -0.494 ~ -5.146 and –0.921 ~ -1.783 GPa, respectively. In average, the stress values evaluated by Raman method are smaller. This may be due to the following reasons. The stress constant used in Raman method varies from 1.70 to 3.05 GPa.cm in literature[3-7], can resulting in a difference in stress value up to ±36%. The X-ray elastic constants used in calculation in XRD method may not be the typical data for films deposited under different deposition conditions. The laser beam of micro Raman spectrometer is around 10 μm in size and its penetration depth is very limited; therefore, the stress so evaluated is stress close to surface of the films.

3.3 Effect of film thickness on residual stress

Figure 2 shows effect of film thickness on residual stress in the (111) textured diamond films on silicon substrate. The residual stress is compressive in nature and was determined by Clemens-Bain method[2]. At thickness around 12 μm, it revealed a maximum compressive stress. At thickness beyond 12 μm, the compressive stress is less for a thicker film. This may relate to a lower non-diamond carbon content in diamond crystals near surface side of the thick film. At thickness below 12 μm, diamond crystallites are smaller and not so dense, and are surrounded by more grain boundary non-diamond phases. Therefore, contribution from the intrinsic stress due to non-diamond content in diamond crystallites is not a dominant factor in determining the stress state of the films.

4. CONCLUSIONS

The stress states and quality of diamond films can be evaluated nondestructively by three different methods. In this case, Clemens-Bain method is for the (111) textured films. The Rietveld XRD-pattern refining method can result in a significant improvement in stress evaluations. The Raman method is for determining the stress state close to the surface of the film. The Clemens-Bain method is good for evaluating the stress state of a textured film. The three nondestructive methods for evaluating the stress state in diamond films can be further refined by considering the stress constant in Raman method and X-ray elastic constants in XRD methods are function of deposition conditions. The origins of the residual stress in diamond films are mainly the sum of thermal stress and intrinsic stress. 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 carbon content will result in a larger compressive stress.

5. REFERENCES

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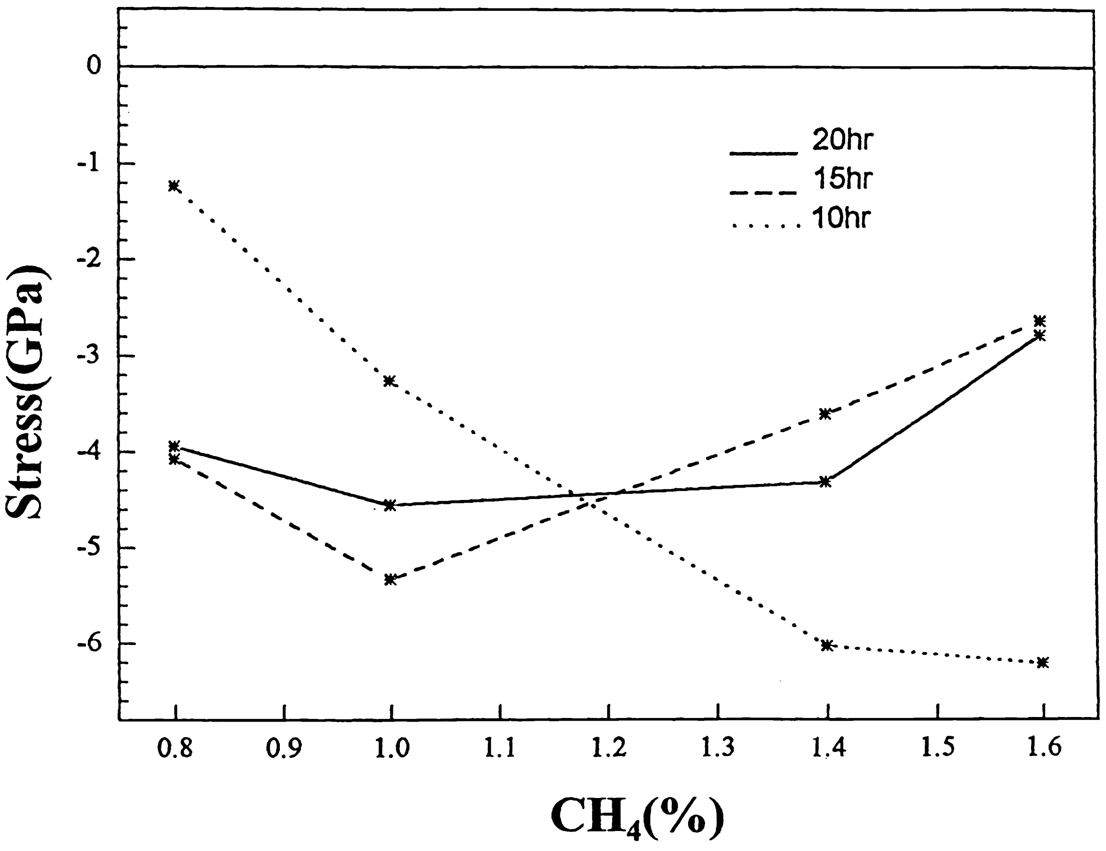
Table 1: Comparison of different evaluation methods on the residual stresses of diamond films on silicon wafer , i.e. Raman spectroscopy (σ_R), LIBAD (σ_L) and Clemens-Bain method (σ_{CB}); the intrinsic stress ($\sigma_{R/in}$) and deposition conditions are also shown.

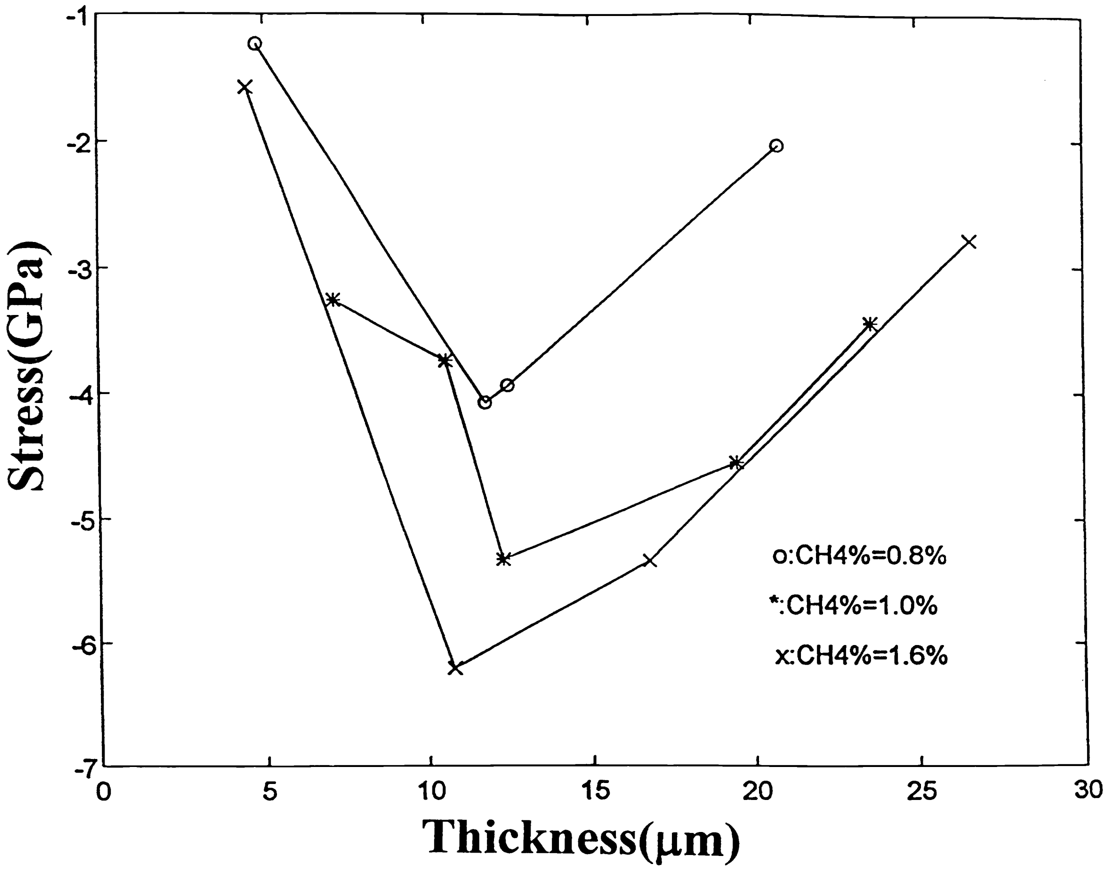
Sample No (substrate)	Thickness (μm)	$\sigma_{R/in}$ (GPa)	σ_R (GPa)	σ_L (GPa)	σ_{CB} (GPa)	Deposition conditions#: *CH_4/H_2 ratio; substrate temp.(°C); dep. time(hr)*
C29(Si)	10.6	-3.481	-1.437	-0.752	-3.071	1.0/100; 750; 10
C30(Si)	14.6	-3.348	-1.129	-4.243	-5.146	1.2/100; 750; 15
C32(Si)	12.5	-3.684	-1.010	-2.845	-0.494	0.8/100; 700; 20
C33(Si)	24.8	-2.891	-1.137	-2.578	-2.356	1.2/100; 700; 20
C34(Si)	11.8	-3.817	-0.942	-2.039	-2.380	0.8/100; 700; 15
C35(Si)	12.3	-5.169	-1.485	-1.006	-2.547	1.0/100; 700; 15
C36(Si)	19.5	-4.296	-1.783	-2.579	-2.667	1.0/100; 700; 20
C41(Si)	20.8	-4.051	-1.526	-1.518	-1.191	1.4/100; 700; 20
C42(Si)	7.5	-1.546	-1.357	-2.197	-2.619	1.4/100; 700; 10
C43(Si)	13.3	-2.369	-0.921	-0.750	-1.729	1.4/100; 700; 15
C47(Si)	4.5	-1.310	-1.729	-3.668	-4.037	1.6/100; 700; 5

Filament temperature = 2350°C; total pressure = 30 torr; the substrate was polished with 1 μm diamond paste before diamond deposition.

List of Table and Figures



Stress(GPa)
0
-1
-2
-3
-4
-5
-6
20hr
15hr
10hr
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
CH4(%)



Stress(GPa)
-1
-2
-3
-4
-5
-6
-7
0
5
10
15
20
25
30
Thickness(μm)
o:CH4%=0.8%
*:CH4%=1.0%
x:CH4%=1.6%