An advanced method for measuring the residual stress of deposited film utilizing laser spallation technique

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Abstract

Residual stress of thin diamond films deposited by chemical vapor deposition (CVD) method was measured using a new method for residual stress measurement we developed. Compressive residual stresses of CVD diamond films were determined from the height and diameter of protuberance of film delaminated by pulse laser spallation technique. We produced the protuberance with different diameter and height by changing the laser energy. Compressive stresses were calculated from the momentum balance of atmospheric pressure and internal compressive force of the film. The residual stress of the well-faceted diamond film was measured as $-338\pm22$ MPa and agreed well with the stress ($-348\pm17$ MPa) measured by the X-ray diffraction method. In three other polycrystalline diamond films with different grain structure, the compressive stresses decreased from 300 to 147 MPa with decreasing the grain size from a few microns to tens of nanometers. Small compressive stresses of fine grain films are correlated with the grain boundary structure according to visible Raman spectra study conducted.

Keywords: Laser spallation; Residual stress; CVD diamond film; Grain boundary structure

1. Introduction

Residual stress of surface films deposited by chemical and physical vapor deposition method (CVD and PVD) causes film damages such as deformation, decohesion and often leads to the deterioration of functionality of the film. For the titanium nitride or diamond coated cutting tools produced by CVD method, both the adhesion strength and residual stress determine the reliability and life of the products. Quantitative measurement of the strength and residual stress are important for the optimization of the deposition condition.

We previously developed a modified pulse laser spallation method to measure the adhesive strength of the film. Here, a strong expansion pulse wave was produced by the break-down of a confined oil layer on the opposite surface of the film substrate and produced a small delamination. Adhesion strength can be determined from the particle velocity of the film at the threshold pulse laser energy to cause a small delamination. Recently, we found that the delamination generated protuberance caused by compressive residual stress in the film. Residual stress can be measured from both the height and diameter of a relatively large protuberance. This method can measure the residual stress without knowing the elastic property of the film and is applicable to the film with poor crystallinity, to which conventional X-ray diffraction method cannot be used.

Residual stresses of thin diamond films have been evaluated so far by the curvature method [1–3], X-ray diffraction (XRD) [4–6] and Raman peak shift method [7–10]. These methods, however, possess following problems. The curvature method cannot be used when the substrate is deformed at high deposition temperatures [1]. XRD method needs a sufficient number of diffraction peaks over high diffraction angles, but such peaks are absent for strongly textured films and thin films. The method utilizing the Raman peak shift is not applicable for the nanometer-sized polycrystalline diamond film, to which sharp peaks cannot be obtained.

The method we utilize in this report is an application of laser spallation technique [12,13] and is free from any problems of the conventional methods. It can measure the compressive residual stress of extremely thin films with strong epitaxiality or poor crystallinity. The adhesion strength or residual stress of the deposited film can be measured by producing an extremely small or a relatively large protuberance, respectively.
2. Experimental and analysis procedure

2.1. Pulse laser spallation to produce the delamination

Pulse laser spallation was originally proposed by Vossen [11] to measure the adhesive strength of coated or deposited film in a non-contact manner. We previously modified this method so as to produce strong expansion pulse wave. Fig. 1(a) shows the modified laser spallation method [12,13]. Spallation or delamination of the film is induced by a strong expansion stress wave produced by break-down of an energy-absorbing layer (silicone grease containing MoS2 particles) confined on the opposite surface of the film substrate.

The break-down was induced by a high-energy Q-switched Nd:YAG laser (New Wave Research, Tempest 300, maximum energy, 300 mJ; pulse duration, 3–5 ns; wavelength, 1064 nm). We succeeded in producing the large expansion wave to produce a film delamination as shown in (b).

For the adhesive strength of the film (\(\sigma_{ad}\)), we measured the out-of-plane displacement (\(u\)) by a laser interferometer at the critical laser energy to cause a first small delamination. The adhesive strength of the film was computed by Eq. (1). Detail of this method can be found elsewhere [12],

\[
\sigma_{ad} = -\rho V_l \frac{\partial u(t)}{\partial t}
\]

where \(\rho\) is the density of the medium and \(V_l\) denotes the velocity of the longitudinal wave. \(\rho\) and \(V_l\) of sintered SiC substrate are taken as 3150 kg/m^3 and 11,803 m/s, respectively.

For the residual stress measurement, we produced relatively large delamination with diameter from 1 to 2 mm by increasing the laser energy. Delaminated film bulged out by compressive residual stress. Three-dimensional shape of the protuberance was measured by a scanning laser interferometer at the vertical resolution of 0.1 nm. The height was generally in the range 250–700 nm, and small compared to the diameter of protuberance.

2.2. Specimen

Polycrystalline diamond films were deposited by hot filament CVD method using gas of CH4/N2/H2 mixture on disc-shaped sintered SiC substrate with a diameter of 25.4 mm and thickness of 6 mm. Prior to the deposition operation, substrate surface were scratched using a diamond wheel with particle size of 74 μm to obtain a good adhesion of the film by mechanical anchor effect. Average surface roughness (Ra) was measured as 0.26 μm. Ultrasonic seeding was performed using 4–6 nm diamond powder suspended in ethanol before depositions. This pretreatment enhanced nucleation number to be more than 10^{10} cm\(^{-2}\). We prepared four types of diamond film by changing both the flow rate of N2 gas and deposition temperature. Total gas pressure was kept at 6.7 kPa during deposition. Multiple tantalum filaments with 0.4 mm diameter were heated to decompose the source gases. The SiC substrate was also heated by the hot filaments. Deposition conditions are listed in Table 1. For three specimens: Types-A, B and C, the flow rate of N2 gas was changed from 0 to 1.0 sccm, keeping the filament temperature at 2423 K. The substrate temperature for this condition was at 1043 K. The N2 gas was utilized to enhance the re-nucleation rate and then to produce the diamond films with different structures. Type-D film was deposited at filament temperature of 2273 K and substrate temperature of 893 K. Surface SEM images of four diamond films are compared in Fig. 2. Type-A film shows well faceted diamond grains with grain size of 5–10 μm, indicating good crystallinity. Type-B sample deposited with 0.4 sccm N2 gas additive shows a number of re-nucleation of 2–3 μm grains. Type-C film with 1.0 sccm N2 gas is composed of 10–60 nm grains. Surface morphology of Type-D at substrate temperature 893 K is similar to that of Type-C. Low substrate temperature, however, decreased the deposition rate from 0.83 μm/h (Type C) to 0.36 μm/h (Type D).

The surfaces of the deposited diamond films were mirror polished to accurately measure the delamination geometry by the interferometer. The thickness values (t) of the diamond films in the Table 1 are those after being polished.

2.3. Estimation procedure of residual stress

Compressive residual stress (\(\sigma_R\)) was obtained from the geometry of the delamination. Fig. 3 shows a mechanics model for residual stress measurement. Fig. 3(a) represents a plan view and Fig. 3(b) the cross section of the delaminated film with radius \(a\) and height \(h\). This model represents a circular disk embedded into a circular hole with a slightly smaller diameter. Thus the center of the plate bulges out by a height of \(h\). Next, we consider momentum balance at \(Q\) to the stress \(\sigma_R\).
and atmospheric pressure $p$. Here, the space at the delaminated interface is considered as vacuum, thus the atmospheric pressure $p$ is working on the entire surface of the film. Vertical force by $p$ balances the reaction force $R$ acting along the circular boundary. When the $h$ is small compared to the delamination radius $a$, the moment of the rotational restraint by plate bending is negligible. Momentum balance around point $Q$, is given by Eq. (2).

$$M_1 + M_2 = -2\pi \int_{0}^{a} \sigma_R th \, d\theta + \int_{0}^{2\pi} pr(a-r) \, d\theta \, dr = 0$$  \hspace{1cm} (2)

$\sigma_R$ is calculated by Eq. (3).

$$\sigma_R = \frac{pa^2}{6th}$$  \hspace{1cm} (3)

The residual stress can be determined by measuring $h$ and $a$. It is noted that this method does not need any elastic property of the film.

Residual stress is also released by the elastic deformation of the protuberance because thin films cannot support compressive stress. The residual stress correlates with delamination diameter. We calculated the amount of released stress from the strain: $(l' - l)/l$ of film protuberance. Here, $l'$ designates the total length of the delaminated film through the top and $l$ the delamination diameter. Released elastic stress ($\sigma_d$) is calculated by Eq. (4) assuming the plane state of stress.

$$\sigma_d = \frac{E_f}{1-\nu_f} \frac{l' - l}{l}$$  \hspace{1cm} (4)

where $E_f$ and $\nu_f$ are Young’s modulus (1050 GPa) and Poisson’s ratio (0.09) of the diamond, respectively [14]. Fig. 4 shows the calculated stress $\sigma_d$ for Type-B film as a function of delamination diameter ($2a$). $\sigma_d$ is found to be less than 1.0 MPa and negligible compared to the large residual stress. Thus, we ignore $\sigma_d$ in calculating the residual stress of the diamond film ($\sigma_R$).

3. Results and discussion

Very small delaminations, detectable by acoustic emission method [13], occurred at the critical laser energy of 55.0 mJ for Type-A, 53.8 mJ for Type-B, 58.0 mJ for Type-C and 47.9 mJ for Type-D film. Interfacial adhesive strength was estimated as 300 MPa for Type-A, 290 MPa for Type-B, 310 MPa for Type-C and 285 MPa for Type-D. No significant difference was observed in the adhesive strength in spite of large change of deposition method and consequently the film structure.
We next produced relatively large delamination using higher laser energies. Fig. 5 shows optical microscopic images (left) and cross-sectional profile of protuberance (right) for Type-A film as a function of laser energy. Both the diameter $2a$ and the height $h$ increased with increasing the level of laser energy. Laser spallation at 59 mJ produced a micro-crack in the delaminated diamond film. This blister shows an extremely high height, 3.5–9.8 times larger than that of another blister without micro-crack. This protrusion in the upper direction is produced by the impregnation of through the crack.

The residual stresses of four films, calculated by Eq. (3), were plotted as a function of the film thickness in Fig. 6. Here, the horizontal axis represents $2a/t$ in order to compare the effect of film thickness. The residual stress of Type-A diamond film was measured as $\sigma_{R} = 338 \pm 22$ MPa. In three other polycrystalline diamond films with different grain structure, the compressive stresses decreased from 300 MPa for Type B, 259 MPa for Type C, and 147 MPa for Type D. It is noted that the calculated stress values are independent of $2a/t$ and the compressive residual stress decreases in the order of Type-$A \rightarrow B \rightarrow C \rightarrow D$. This implies that the compressive residual stress decreases as grain size decreases (Types-$A$, $B$ and $C$) and much larger decreases were found when the film was produced at low substrate temperature (Type-$D$).

In order to verify the utility of the proposed method, we measured the residual stress of the Type-$A$ film by $d_{\psi}$-$\sin^{2}\psi$ method of X-ray diffraction (XRD) and compared it with that by the proposed method. The XRD method could measure the residual stress of only Type-$A$ film with well faceted grains. We utilized a high resolution X-ray diffractometer (Philips X’Pert MRD) with a Cu X-ray tube. This method allows the determination of the residual stress averaged over whole depth due to the transparency of X-ray into the diamond [15]. The residual stress can be obtained through Eq. (5) by measuring the lattice spacing $d_{hkl}$ at different tilt angles $\psi$.

$$\frac{d_{\psi} - d_{0}}{d_{0}} = 1 + \frac{\nu}{E} \sigma_{R} \sin^{2}\psi$$  \hspace{1cm} (5)$$

where $E$ and $\nu$ are the Young’s modulus and the Poisson’s ratio of the film, respectively. The same value of $E$ and $\nu$ used in Eq. (4) were taken into the calculation. $d_{0}$ is the stress free lattice spacing. Diffraction peaks of (331) lattice plane ($d_{0} = 81.803 \text{ pm}$) were measured since lattice planes with higher Miller indices ($hkl$) are much sensitive to the residual stress. Nevertheless, both the intensity of the (331) peak and peak shift by residual stress are very weak and small due to the extremely high stiffness of the diamond. Diffraction peaks cannot be obtained for Types $B$, $C$ and $D$ film possibly due to poor crystallinity. We measured the (331) peak of Type-$A$ film by changing the angle $\psi$ between 10 and 75°. Fig. 7(a) shows the (331) scan between 138 and 144° at $\psi = 0$ degree. We obtained smooth peak profiles by taking 40 s for each 0.02 scan step. Two peaks of the $K\alpha_{1}$ and $K\alpha_{2}$ lines were successfully decomposed using Gaussian curve fitting and only the central peak position of the $K\alpha_{1}$ line was submitted to the measurement. The lattice spacing $d_{\psi}$ was then calculated and plotted as a function of the $\sin^{2}\psi$, as shown in the Fig. 7(b).
The linear and negatively declined line indicates a homogeneous compressive stress in the film. The residual stress was calculated as $-348 \pm 17$ MPa. This value agrees well with that ($-338 \pm 22$ MPa) obtained by the method proposed.

Next, we studied the structural detail of the CVD diamond films by visible laser Raman spectroscopy. A laser light with wavelength in the visible region was utilized. This type of Raman spectroscopy has been widely used to examine the crystallinity of carbon film consisting of sp$^2$- and sp$^3$-bonded carbon. The intensity of the peaks for sp$^3$-bonded carbon, is much larger than that of sp$^3$-bonded carbon since the energy of the incident photons is much lower than that of the band gap for sp$^3$-bonded carbon [16]. The visible laser Raman spectra of the polycrystalline diamond film are often characterized by six peaks at 1150, 1200, 1350, 1333, 1450 and 1580 cm$^{-1}$. The peak at 1333 cm$^{-1}$ is the first-order Raman spectrum of diamond lattice. The peaks at 1350 and 1580 cm$^{-1}$ are understood as graphitic phase which is called as the D-band and G-band, respectively. The D-band is attributed to a breathing mode of sp$^2$-bonded carbon with $A_{1g}$ symmetry [7,17,18], and G-band is attributed to stretching mode of sp$^2$-bonded carbon with the $E_{2g}$ symmetry [19]. Some studies attributed the peaks at $\sim 1200$ cm$^{-1}$ as the C–N vibration [20,21]. The origins of the peaks at $\sim 1150$ and $\sim 1450$ cm$^{-1}$

![Fig. 6. Residual stress vs. delamination diameter for four types of CVD diamond film.](image)

![Fig. 7. X-ray diffraction stress measurement result ($d_{\psi\gamma}-\sin^2\psi$ method) for Type-A specimen. (a) (331) diffraction peak at $\psi=0$ degree; (b) $d_{\psi\gamma}-\sin^2\psi$ plot.](image)
are yet to be clarified although the attribution to nanometer size diamond grain has been supported widely [22–24]. However, this assignment has been denied by Ferrari et al. who claim those peaks for sp²-bonded carbon [25]. Their studies are more convincing.

Polycrystalline diamond films are composed of sp³-bonded diamond grain and a mixture of disordered sp² and sp³ bonded grain boundary carbon including a number of defects [26]. We measured the visible laser Raman spectra (RENISHAW, RAMASCOPE SYSTEM 1000; 515 nm laser) of the four specimens. Results are shown in Fig. 8. The spectra were decomposed to six spectral component of Gaussian curve after subtraction of the photoluminescence background. We observed a distinct difference between four spectra. For the spectra of Types-A, B and C, relative intensity or integration of the peak at \(1333 \text{ cm}^{-1}\) assigned to sp³-bonded carbon (diamond), against those of peaks assigned to sp²-bonded carbon (non-diamond), decreased with decrease in grain size. The reason for lower compressive residual stress of Types B and C is due to an increase of sp² bonded grain boundary phase (graphite). The sp² bonded grain boundary phase is known to have elastic constant smaller than that of diamond. Thermal expansion coefficient of the sp² bonded grain boundary phase is larger than that of diamond phase. Sufficient lower stress of Type-D might be explained by intensity difference assigned to non-diamond phases. It is, however, difficult to discuss the structural difference from peaks non-assigned to non-diamond phase. Lower residual stress in Type-D film is more likely considered to be produced by the lower deposition temperature.

4. Conclusion

Important findings obtained in this study are summarized below.

(1) A new and simple method to measure the compressive residual stress of diamond films is developed. It uses only the diameter and height of protuberance of delaminated film produced by pulse laser spallation technique.

(2) Protuberance of different diameter was successfully produced by changing the laser pulse energy. Bulge height increased with delamination diameter. These are used to determine the residual stress.

(3) The residual stress of the well-faceted Type-A diamond film is estimated to be \(-338 \pm 22\) MPa, in good agreement with that measured by the X-ray diffraction stress analysis method.

(4) Fine grain diamond films possess lower compressive residual stresses of 300–147 MPa, which can be explained by grain boundary structure with more non-diamond bonding as determined by Raman spectra.

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References

[1] L. Schafer, X. Jiang, C.P. Klages, In-situ measuring of stress development in diamond thin films, in: Y. Tzeng, M. Yoshikawa, M. Murakawa, A. Feldman (Eds.), Applications of Diamond Film and Related Materials, Elsevier, Amsterdam, 1991, pp. 121–128.

[2] J.G. Kim, J. Yu, D.H. Cho, Y.J. Baik, Calculation of intrinsic stress by creep deformation of an Si substrate on chemical vapor deposited diamond films, Diamond Relat. Mater. 9 (1) (2000) 61–66.

[3] J. Yu, J.G. Kim, J.O. Chung, D.H. Cho, An elastic/plastic analysis of the intrinsic stresses in chemical vapor deposited diamond films on silicon substrates, J. Appl. Phys. 88 (3) (2000) 1688–1694.

[4] S.K. Choi, D.Y. Jung, H.M. Choi, Intrinsic stress and its relaxation in diamond film deposited by hot filament chemical vapor deposition, J. Vacum Sci. Technol. A14 (1996) 165–169.

[5] J.G. Kim, J. Yu, Measurement of residual stress in diamond films obtained using chemical vapor deposition, Jpn. J. Appl. Phys. 37 (7B) (1998) L890–L893.

[6] J.A. Baglio, B.C. Farnsworth, S. Hankin, G. Hamill, D. O’Neil, Studies of stress related issues in microwave CVD diamond on 100 silicon substrates, Thin Solid Films 212 (1992) 180–185.

[7] D.S. Knight, W.B. White, Characterization of diamond films by Raman spectroscopy, J. Mater Res. 4 (2) (1989) 385–393.

[8] L.I. Vlasov, V.G. Ratchenko, E.D. Obraztsova, A.A. Smolin, V.I. Knov, Stress mapping of chemical-vapor-deposited diamond film surface by micro-Raman spectroscopy, Appl. Phys. Lett. 71 (13) (1997) 1789–1791.

[9] N.S.V. Damme, D.C. Nagle, S.R. Winzer, Stress in thick diamond films deposited on silicon, Appl. Phys. Lett. 58 (25) (1991) 2919–2920.

[10] J.W. Anger, D.K. Veirs, G.M. Rosenblatt, Spatially resolved Raman studies of diamond films grown by chemical vapor deposition, Phys. Rev. B 43 (8) (1991) 6491–6499.

[11] J.L. Vossen, Measurements of film–substrate bond strength by laser spallation adhesion measurement of thin films, in: K.L. Mittal (Ed.), Thick Films and Bulk Coatings, ASTM, 1978, pp. 122–133.

[12] R. Ikeda, S. Tasaka, H. Cho, M. Takemoto, Evaluation of adhesive strength of chemical vapor deposition films by laser spallation, Jpn. J. Appl. Phys. 43 (58) (2004) 3123–3126.