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Determination of biaxial modulus of chemical vapor-deposited diamond films

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Abstract

A new approach for determining the biaxial modulus of chemical vapor-deposited diamond films is presented, with an example of diamond coating on copper substrate. The biaxial modulus of the film and substrate are calculated from a combination of bimetal and plate bending theories. To realize a valid calculation, residual stresses in the film and the curvature radius of the sample need to be known independently. Raman spectroscopy is employed to evaluate residual stress and a laser displacement meter is used to measure the sample deflection. Raman spectra of the as-grown diamond show that the film is under a compressive stress of −5.1 GPa, while the corresponding freestanding film obtained by etching off the metal substrate is nearly stress-free. The sample surface is almost flat before the diamond coating, while the curvature radius becomes 124 mm after diamond deposition. The biaxial modulus calculated for the diamond film is approximately 995 GPa. This implies that the diamond film is of relatively high quality, which is confirmed by its Raman spectra. Interestingly, the biaxial modulus calculated for the copper substrate is much lower than the value given in the literature. This is attributed to plastic deformation of the substrate. A concept of equivalent modulus is discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Diamond film; Biaxial modulus; Stress; Raman spectroscopy

1. Introduction

The superior properties of chemical-vapor-deposited (CVD) diamond films make them attractive in many potential applications [1–4]. The elastic modulus is a basic property directly describing the bonding strength and structure of the material. For example, in CVD diamond, the fraction of sp^3 and sp^2 carbon bonds strongly depends on the process. Such variation in the film structure significantly modifies the elastic properties of resultant films [5]. Therefore, effective evaluation of the elastic modulus is essentially desired.

A number of techniques have been employed to characterize the elastic modulus of CVD diamond. These techniques include: ultralow-load indentation tests [6–12]; short laser-pulse diagnostics [5,13]; ultrasonic resonance techniques [14]; bending tests [15–17]; bulge tests [18–21]; vibrating-membrane methods [22]; surface acoustic wave spectroscopy [23,24], etc. Each of these techniques possesses unique and diverse advantages, but with limitations in one or more specific aspects, such as complicated sample preparation, dependent on the film morphology, and so on. This is probably one reason that the values reported for the elastic modulus of CVD diamond fall in a wide range [6–24], although the samples used by the authors might be somewhat different.

In this paper, we propose a new method to determine the biaxial modulus of CVD diamond film from a combination of bimetal and plate bending theories. A pre-condition to realize a valid calculation for the biaxial modulus is that residual stresses in the film and the curvature radius of the sample must be known indepen-

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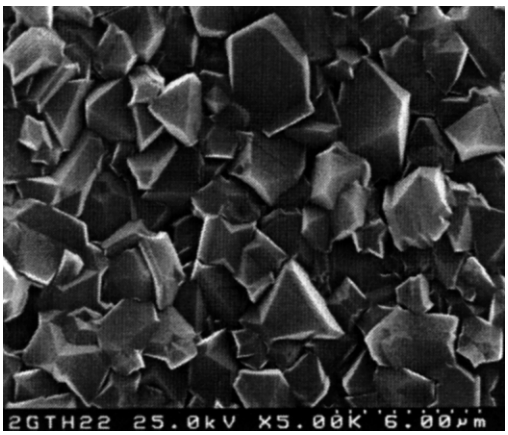


Fig. 1. A typical SEM image of the diamond film grown on the Ti pre-coated copper substrate. The film shows dominant (111) faces.

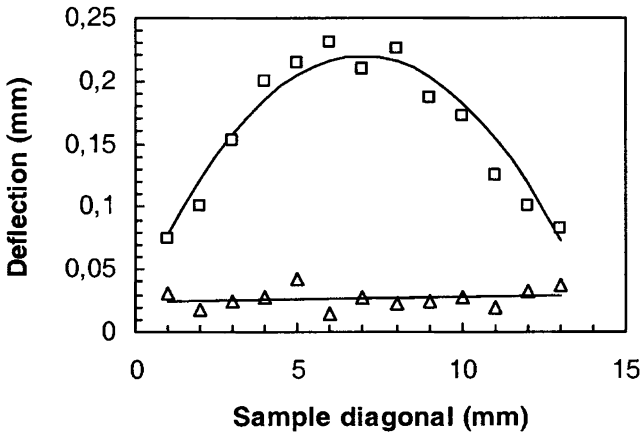


Fig. 2. The sample deflection measured before the diamond deposition (Δ) and after the diamond coating (□).

dently. Raman spectroscopy has been the most common technique for characterizing CVD diamond. Thus, residual stresses can be readily evaluated from the diamond Raman-line shift [25,26]. Furthermore, the sample curvature can usually be measured with high accuracy. Therefore, our new method is simple and easy to conduct.

2. Experimental details

The substrates used for diamond deposition were polycrystalline copper foil (99%) of 1 mm in thickness and 10×10 mm^2 in size. They were first polished with a sequence of SiC sandpapers down to 600# grid, then ultrasonically cleaned in acetone for 10 min and dried in an oven at 100°C for 15 min. A titanium layer of approximately 0.2 μm in thickness was deposited on the substrate by DC magnetron sputtering prior to diamond coating to enhance adhesion [27]. Diamond synthesis was conducted using an ASTeX 2.45-GHz microwave plasma CVD system. The process gases were hydrogen (H_2) and methane (CH_4). The deposition parameters employed were as follows: microwave power, 2800 W; gas pressure, 90 torr; total gas flow rate, 424 sccm, consisting of 400 sccm H_2 and 24 sccm CH_4; deposition temperature, ~750°C; and deposition time, 2 h. Diamond films prepared under these conditions exhibited a so-called 'white grade' high quality, as has been reported previously [27].

The film morphology was observed using a Hitachi 4100 scanning electron microscope (SEM). A Jobin Yvon 64000 Raman spectrometer with a 514-nm Ar^+ ion laser was used to characterize the diamond film quality and, by the shift of the diamond peak, the stress present in the film. A type IIa bulk diamond was used to calibrate the diamond Raman line position. The sample curvature was measured using a Keyence 2100 laser displacement meter.

3. Results and discussion

Diamond film with a thickness of 3.4 μm was deposited on the titanium pre-coated copper substrate. Fig. 1 shows a typical SEM image of the film, which exhibits clear crystallinity with dominant (111) faces. The sample deflection, as shown in Fig. 2, was measured before and after diamond deposition. It is evident that the sample was almost flat before diamond deposition. However, after being coated with the diamond film, the curvature radius of the sample was deduced to be approximately 124 mm, with the film on the convex side. Details on the deduction of the curvature radius from the deflection measurement have been described in [28].

Raman spectra as shown in Fig. 3 confirm that the film was of high quality. The as-grown film exhibits a diamond Raman peak located at 1341 cm^{-1}. Raman line splitting is not obvious. It is known that the Raman

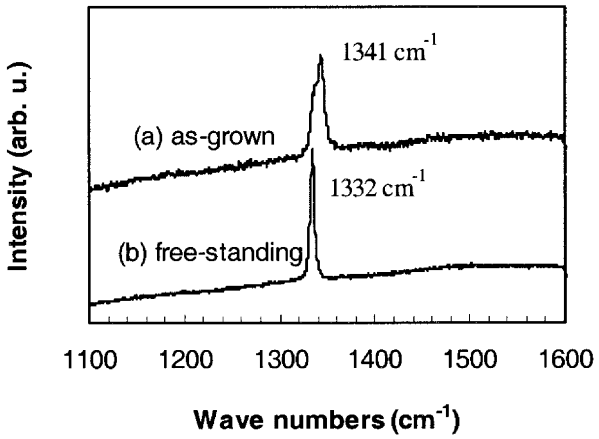


Fig. 3. Raman spectra of the diamond film deposited on Ti pre-coated copper substrate: (a) as-grown film; and (b) free-standing film obtained by etching off the metal substrate.

shift is proportional to the magnitude of biaxial stress (σ) in diamond film, with relationships as follows [26]:

$$\sigma = -1.08(\nu_s - \nu_0)\ \text{(GPa) for a singlet phonon} \quad (1)$$

$$\sigma = -0.384(\nu_d - \nu_0)\ \text{(GPa) for a doublet phonon} \quad (2)$$

where $\nu_0 = 1332\ \text{cm}^{-1}$, ν_s is the observed maximum of the singlet in the spectrum and ν_d the maximum of the doublet. Since splitting of the Raman line is not obvious in our film, the observed peak position ν_m can be assumed to be located at the center between the singlet ν_s and doublet ν_d, i.e. $\nu_m = \frac{1}{2} \times (\nu_s + \nu_d)$ [29]. From Eqs. (1) and (2) we obtain:

$$\sigma = -0.567(\nu_m - \nu_0)\ \text{(GPa) for an unsplit peak} \quad (3)$$

Therefore, biaxial stress in the film is deduced to be approximately -5.103 GPa in compression.

After curvature and Raman spectrum measurements, the metal substrate was etched off using nitric acid in order to obtain a free-standing diamond film. Raman spectra measured from the free-standing film show a single diamond peak at approximately 1332 cm^{-1} (see Fig. 3). This implies that intrinsic stress in the film was very small [refer to Eq. (3)] as compared with the total residual stress evaluated from the Raman spectrum of the as-grown film. We therefore deduce that the residual stress in our diamond film was mainly due to contributions from thermal stress.

Applying the bimetal theory to our sample [30], the curvature radius R can be expressed by:

$$\frac{1}{R} = \frac{6(\alpha_s - \alpha_f)(T_d - T_r)(1+m)^2}{h\left[3(1+m)^2 + (1+mn)\left(m^2 + \frac{1}{mn}\right)\right]} \quad (4)$$

$$m = \frac{d_f}{d_s} \quad (5)$$

$$n = \frac{Y_f}{Y_s} \quad (6)$$

$$h = d_f + d_s \quad (7)$$

where α_s and α_f are the thermal expansion coefficients for copper and diamond, respectively, $T_r = 25°\text{C}$ is room temperature and $T_d = 750°\text{C}$ is the deposition temperature, $d_s = 1$ mm and $d_f = 3.4$ μm are the substrate and film thickness, respectively, and Y_s and Y_f are the biaxial modulus for copper and diamond, respectively. It should be noted that in the bimetal theory, the thermal expansion coefficients, α_s and α_f, are usually considered as constants. However, it is known that copper and diamond have temperature-dependent expansion coefficients in the range of 25 (room temperature) to 750°C (deposition temperature). Therefore, to accurately calculate the curvature radius R, Eq. (4) should be modified as:

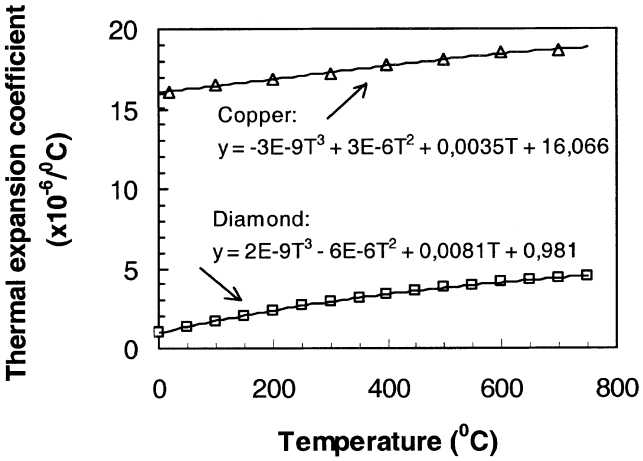


Fig. 4. Thermal expansion coefficients α_f and α_s for diamond and copper. Symbols □ and Δ represent data from [30,31]. Continuous lines are from the best fits.

$$\frac{1}{R} = \frac{6(1+m)^2 \int_{T_r}^{T_d} (\alpha_s - \alpha_f)\mathrm{d}T}{h\left[3(1+m)^2 + (1+mn)\left(m^2 + \frac{1}{mn}\right)\right]} \quad (8)$$

From [31,32], we obtain α_s and α_f data for copper and diamond, as shown in Fig. 4. Fitting the data, we obtain the temperature-dependent relationships for α_s and α_f as follows:

$$\alpha_s = 16.066 + 3.5 \times 10^{-3} T + 3 \times 10^{-6} T^2 - 3 \times 10^{-9} T^3 \quad (9)$$

$$\alpha_f = 0.981 + 8.1 \times 10^{-3} T - 6 \times 10^{-6} T^2 + 2 \times 10^{-9} T^3 \quad (10)$$

Thus, the integral in Eq. (8) can be calculated.

From the plate bending theory [30,33], biaxial stress σ in the film can be expressed by:

$$\sigma = \frac{1}{R}\left[-\frac{Y_f d_f^3 + Y_s d_s^3}{6 d_f (d_f + d_s)} + Y_f\left(x - \frac{d_f}{2}\right)\right] \quad (11)$$

where x is the distance from the film/substrate interface, as shown in Fig. 5. Eq. (11) indicates that the biaxial stress σ changes linearly from the film/substrate interface to the film surface, i.e. $\sigma = ax + b$, where $a = \frac{Y_f}{R}$ is the stress variation rate and $b = -\frac{1}{R} \times \left[\frac{Y_f d_f^3 + Y_s d_s^3}{6 d_f (d_f + d_s)} + Y_f \frac{d_f}{2}\right]$ is the stress at the film/substrate interface. The biaxial modulus value for a CVD diamond film is usually lower than the value for bulk diamond ($\sim$1129 GPa). Remember that the sample curvature radius is 124 mm, and the stress variation rate a is therefore estimated to be lower than 0.009 GPa μm^{-1}. This

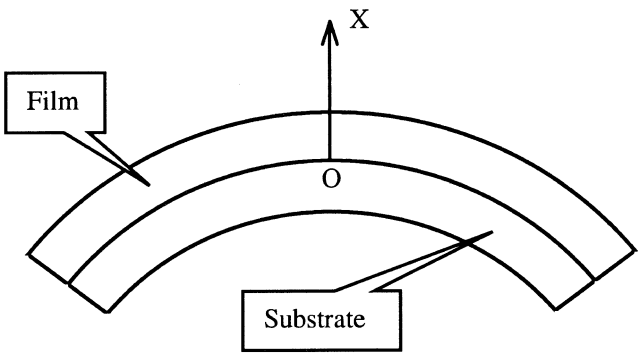


Fig. 5. An illustration of the bimetal plate.

implies that the stress difference along the film depth (3.4 μm in thickness) is smaller than 0.03 GPa. This value is small and is negligible compared to the residual stress value (5.1 GPa) deduced from Raman spectra. The idea here is that we can use a mean stress to represent the stress in the film, while the stress value deduced from the Raman spectra can be considered as the mean stress. From Eq. (11), the mean stress σ_m can be expressed as:

$$\sigma_m = \frac{1}{R}\left[-\frac{Y_f d_f^3 + Y_s d_s^3}{6d_f(d_f+d_s)}\right] \quad (12)$$

In Eqs. (8) and (12), the unknown parameters are Y_f and Y_s. Since the residual stress σ or σ_m and the sample curvature radius R are measured independently, we should expect a set of unique solutions (if they exist) for Y_f and Y_s from the combination of Eqs. (8) and (12). Solving these equations, the biaxial modulus values for the diamond film and the copper substrate are found to be 995 and 13 GPa, respectively.

The Y_f value is in good agreement with literature reports for high-quality CVD diamond film [5]. Raman spectra shown in Fig. 3 indeed indicate that the film quality is fairly good. As a comparison, we calculate the biaxial modulus of bulk diamond, using the Young's modulus (1043 GPa) and Poisson ratio (0.07) given in [1]. The biaxial modulus of the bulk diamond is deduced to be approximately 1120 GPa. Therefore, the quality of our CVD diamond film is only slightly inferior to that of bulk diamond. It is interesting to note that the Y_s value is much lower than the biaxial modulus of 195 GPa for copper given in [34]. We suggest that this is due to plastic deformation that occurs in copper during post-growth cooling. In fact, plastic deformation in copper substrates after CVD diamond coating has been observed by Ralchenko et al. [35]. Therefore, we define the Y_s value calculated as an equivalent modulus. Indeed, we note that Eqs. (8) and (12) are solved without prior knowledge of the elastic properties of either the film or the substrate. Therefore, the equivalent modulus can be used to describe a real material, assuming that the material behaves elastically, while actually both plastic and elastic deformations exist. Obviously, the equivalent modulus value should be lower than the elastic biaxial modulus due to the presence of plastic deformation. This indicates the extent of plastic deformation.

The present model is developed for CVD diamond films with very small elastic deformation when coated onto most substrate materials, such as metal and ceramics. It may also be applied to other thin films and coatings. However, since it calculates the equivalent modulus, the film should usually possess a biaxial modulus much greater than that of the substrate. Also, it requires detailed information on the thermal expansion coefficient as a function of temperature.

4. Conclusions

The biaxial modulus of CVD diamond film deposited on a soft substrate, copper, can be evaluated according to residual stresses in the film and the curvature radius of the sample. Raman spectra show that residual stress in our diamond film is mainly contributed by thermal stress, while intrinsic stress is negligible. Using the bimetal and plate bending theories, valid solutions of the biaxial modulus for the diamond film and the copper substrate are deduced. The value corresponding to diamond was found to be 995 GPa, implying a relatively high-quality film, which is confirmed by Raman spectroscopy. Plastic deformation occurs to a significant extent in the copper substrate, resulting in a modulus of 13 GPa calculated for copper. This value is proposed as an equivalent modulus, which is expected to be much lower than the elastic biaxial modulus.

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