

RESONANCE ULTRASOUND SPECTROSCOPY FOR EVALUATING ELASTIC CONSTANTS AND INCOHESIVE BONDS OF THIN FILMS

N. Nakamura¹, H. Ogi¹, and M. Hirao¹

¹ Osaka University, Osaka, Japan

Abstract: Free-vibration-resonance frequencies of a film/substrate layered specimen depend on the dimensions, densities, and elastic constants both of the film and substrate. Then, the elastic constants of thin films are inversely determined by measuring the resonance frequencies and the other parameters. Because contributions of the film elastic constants to the resonance frequencies are small, high accurate measurement of resonance frequencies is indispensable. In this study, we develop a piezoelectric tripod transducer, which enables one to measure the resonance frequencies with an accuracy better than 10^{-4} . In the inverse calculation, mode identification for measured resonance frequencies is the key issue. We achieve this by measuring the surface-displacement distributions using laser-Doppler interferometry. We applied the proposed method to a thin film of chemical-vapor-deposition diamond. Measured elastic constants are smaller than those of bulk diamond. We attribute the compliant diamond thin film to local incohesive bonds at grain boundaries.

Introduction: Accurate elastic constants of thin films are indispensable to designing and stress analysis of devices. Many studies have clarified elastic properties of bulk materials. However, those of thin films are not well known because of the difficulty of measurements. Thin films are supposed to be elastically different from the bulk and to show elastic anisotropy between the in-plane and out-of-plane directions, even if they are polycrystalline. Anisotropy can be induced by residual stress, texture, columnar structure, and incohesive bonds at grain boundaries. The thin films usually show transverse isotropy and have five independent elastic constants denoted by C_{11} , C_{33} , C_{12} , C_{13} , and C_{44} , where the x_1 and x_2 axes lie in the film plane and x_3 is along the out-of-plane direction. Previous studies measured the thin-film elastic constants using vibrating reed method [1], nanoindentation [2], and Brillouin-scattering method [3]. Most of them assumed thin films to be elastically isotropic and involved ambiguity caused by the mechanical contact needed for gripping the specimen and for the acoustic transduction. In this study we developed an advanced resonance-ultrasound-spectroscopy (RUS) method for measuring the anisotropic thin-film elastic constants. RUS determines elastic constants from dimensions, density, and free-vibration-resonance frequencies of a solid specimen. This method has been applied to many bulk materials [4-7]. In order to apply the RUS method to thin films, high accurate measurement of resonance frequencies and correct mode identification of individual resonance are required. We overcame these difficulties by developing a piezoelectric tripod and measuring surface-displacement distributions of the specimen vibrating at a resonance frequency with a laser-Doppler interferometer. We call this RUS/laser method. Reliability of the RUS/laser method is demonstrated by measuring elastic constants of monocrystal silicon. We then measure chemical-vapor-deposition (CVD) diamond thin films.

RUS/laser method: Resonance frequencies of free vibrations of a film/substrate layered specimen depend on densities, dimensions, and elastic constants of both film and substrate. Thin film's elastic constants are inversely determined by measuring the resonance frequencies and other measurable parameters. For the film/substrate layered specimen, an algorithm using the Rayleigh-Ritz method was established by Heyliger [8].

Rayleigh-Ritz method considers minimization of Lagrangian L ;

$$\delta \int_V L dV = 0 \quad . \quad (1)$$

The integration is taken over the volume of solid, V . The Lagrangian L is given by

$$L = \frac{1}{2} \left(\rho \omega^2 u_i u_i - C_{ij} S_i S_j \right), \quad (2)$$

where ρ denotes the mass density, ω the angular frequency, u_i the displacement along the x_i axis, C_{ij} the elastic constants, and S_i the engineering strain. In the case of the free vibration of rectangular parallelepiped, no analytical solution exists for the displacements. Then, displacement u_i are approximated by linear combination of basis functions ψ_k^i ,

$$u_i(x_1, x_2, x_3, t) = \sum_k U_k^i \psi_k^i(x_1, x_2, x_3, t) e^{i\omega t}. \quad (3)$$

Here, U_k^i denote the expansion coefficients. For layered parallelepiped specimen, discontinuous displacement gradients at the film/substrate interface must be considered. Heyliger [8] used the one-dimensional Lagrangian interpolation polynomials ($\eta_m^i(x_3)$) and power series ($\xi_l^i(x_1, x_2)$) for the thickness direction and in-plane directions, respectively; that is,

$$\psi_k^i(x_1, x_2, x_3) = \eta_m^i(x_3) \xi_l^i(x_1, x_2). \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (1) results in a matrix equation

$$\omega^2 [\mathbf{M}] \{\mathbf{U}\} = [\mathbf{K}] \{\mathbf{U}\}. \quad (5)$$

Here, $[\mathbf{M}]$ denotes the mass matrix associated with the kinetic energy of the system and $[\mathbf{K}]$ denotes the stiffness matrix associated with the strain energy of the system. $\{\mathbf{U}\}$ denotes the eigenvector composed of the expansion coefficients. Thus, the analysis is formulated in an eigenvalue problem and the resonance frequencies (f) are obtained from the eigenvalues of the system ($\omega = 2\pi f$). Thin film elastic constants are inversely determined by comparing the calculated resonance frequencies with measurements using a standard least-squares-fitting procedure.

In order to determine the thin film elastic constants by the above RUS method, we need to measure the resonance frequencies with sufficient accuracy because of low sensitivities of thin-film elastic constants to the resonance frequencies. For this, we developed a piezoelectric tripod consisting of two piezoelectric pinducers and a support pin. Resonance frequencies are measured by putting the specimen horizontally on the tripod. One pinducer generates continuous-wave vibration and the other detects the vibration amplitude. Sweeping the driving frequency makes a resonance spectrum. The resonance spectrum includes many peaks, and fitting the Lorentzian function around these peaks determines the resonance frequencies. Reproducibility of measured resonance frequencies among completely independent measurements is better than 10^{-4} at constant temperature of 30 °C, which is much smaller than contributions of the thin-film elastic constants to the resonance frequencies.

In inverse calculation, correct correspondence of the observed and calculated resonance frequencies is indispensable. If modes of the resonance frequencies are identified, the correct correspondence is attained. However, the mode identification has never been straightforward, because the resonance spectrum includes no mode information. We overcome this difficulty by measuring out-of-plane-displacement distributions using a laser-Doppler interferometer.

Comparison between measured and calculated (with Eq.3) displacement distributions results in unambiguous mode identification.

We evaluate reliability of RUS/laser method using a monocrystal silicon, measuring $5.992 \times 4.492 \times 0.208 \text{ mm}^3$. Figure 1 shows errors between measured and calculated resonance frequencies. Measurements and calculations are in agreement within a 0.2% error. Table I shows measured and previously reported elastic constants of monocrystal silicon. Measured elastic constants are in agreement with those reported by previous studies, which demonstrates availability of the present RUS/laser method.

We applied our method to CVD diamond thin film. CVD diamond thin film is a candidate of surface-acoustic-wave (SAW) devices used at high frequency band [10], because of its very high elastic constants. We measured elastic constants of $3.8 \text{ }\mu\text{m}$ CVD diamond thin film deposited by the hot-filament CVD method on a (100) silicon substrate measuring $18.007 \times 15.004 \times 0.528 \text{ mm}^3$.

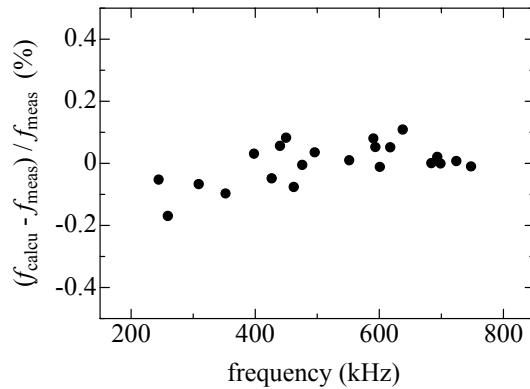


Fig.1 Difference between measured (f_{meas}) and calculated (f_{calcu}) resonance frequencies of monocrystal silicon measuring $5.992 \times 4.492 \times 0.208 \text{ mm}^3$.

Table I Elastic constants of monocrystal silicon determined by the RUS/laser method and previous study (GPa).

	C_{11}	C_{12}	C_{44}
present	164.6	64.1	78.8
ref.9	165.7	63.9	79.6

Results: Figure 2 shows errors between measured and calculated resonance frequencies. After the deposition of the thin film, the resonance frequencies increased by 6%, indicating much higher moduli of diamond than those of silicon. Table II shows determined elastic constants. C_{33} and C_{44} cannot be determined because of their too low contribution to the resonance frequencies. For comparison, we calculated elastic constants of an isotropic polycrystalline diamond by Hill approximation using monocrystal moduli. The calculation represents elastic constants of polycrystalline diamond, which has no texture and includes no incohesive bonds or microcracks. The measured elastic constants are smaller than those of isotropic polycrystalline diamond.

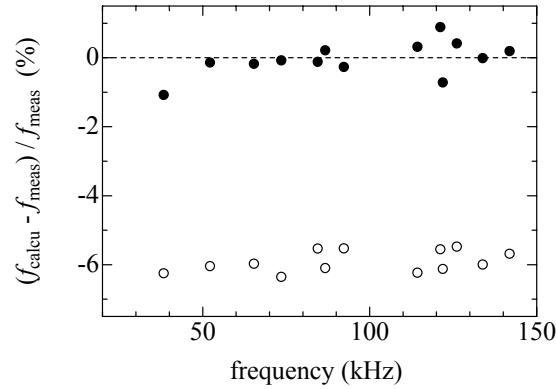


Fig.2 Solid circles indicate the difference between the measured and calculated resonance frequencies of diamond(3.8 μ m)/silicon. Open circles indicate the difference between the measured resonance frequencies of silicon substrate alone and calculated resonance frequencies of diamond(3.8 μ m)/silicon

Table II Measured elastic constants of 3.8- μ m-thick CVD diamond thin film and aggregate elastic constants using monocrystal moduli given in Ref.11.

	aggregate (isotropic)	3.8 μ m
C_{11}	1143.0	1091.9 \pm 17.0
C_{33}	1143.0	-
C_{13}	82.6	294.6 \pm 29.1
C_{12}	82.6	62.8 \pm 12.2
C_{44}	530.2	-
C_{66}^*	530.2	514.6 \pm 21.2
E_1	1131.8	1017.3 \pm 6.8

$$* C_{66}=(C_{11}-C_{12})/2$$

Discussion: We consider three possible factors for the smaller elastic constants than the bulk: (i) residual stress, (ii) texture, and (iii) local incohesive regions. Residual stress changes the interatomic distance and the elastic constants through lattice anharmonicity. However, X-ray-diffraction measurement (Fig.3) indicates the lattice parameter is identical to that of the stress-free monocrystal diamond, suggesting the negligible effect of residual stress, if any. Also, X-ray-diffraction measurement indicates that the diamond thin film has no texture. Therefore, the residual stress and the texture effect cannot be dominant factors for the compliant diamond film.

Finally, we consider the presence of incohesive bonds at grain boundaries. Cross-section SEM observation indicates the columnar grains of the diamond thin films, which possibly contains incohesive bonds at grain boundaries. The origin of such an incohesive bond is not identified, but it could be caused either by microcracks or remaining graphite phase. We estimate this effect using micromechanics calculation assuming that microcracks are included in an isotropic diamond. The calculation detail is described in Ref.11. Calculated elastic constants are C_{11} =1071.6 GPa, C_{66} =498.7 GPa, and E_1 =1064.9 GPa. They are smaller than those of isotropic

diamond, showing the same trend with the measured elastic constants. From the above consideration, we attribute the softening to the incohesive bonding regions at grain boundaries.

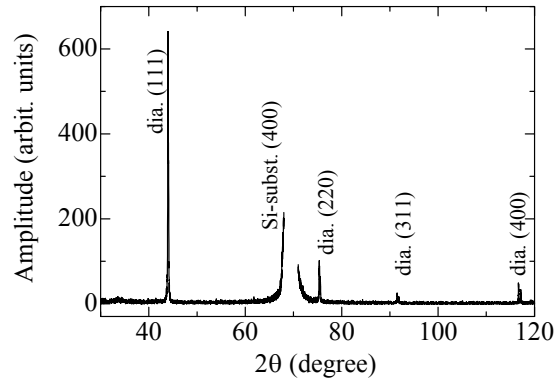


Fig.3 Observed X-ray diffraction spectrum of CVD diamond thin film.

Conclusions: We originally developed the RUS/laser method. The reliability was evaluated by measuring the elastic constants of a monocrystal silicon. Measured elastic constants were in agreement with the previous study. We applied the RUS/laser method to CVD polycrystalline diamond thin film. Measured elastic constants are smaller than those of an isotropic diamond. We attribute the compliant diamond film incohesive bonds at grain boundary. This consideration is supported by X-ray diffraction analysis.

References:

1. H. Mizubayashi, J. Matsuno, and H. Tanimoto, *Scripta Mater.* **41**, 443 (1999).
2. Th. Malkow, I. Arce-García, A. Kolitsch, D. Schneider, S. J. Bull, and T. F. Page, *Diamond Relat. Mater.* **10**, 2199 (2001).
3. P. Djemia, C. Dugautier, T. Chauveau, E. Dogheche, M. I. De Barros, and L. Vandenbulcke, *J. Appl. Phys.* **90**, 3771 (2001).
4. I. Ohno, *J. Phys. Earth* **24**, 355 (1976).
5. A. Migliori, J. L. Sarrao, W. M. Visscher, T. M. Bell, M. Lei, Z. Fisk, and R. G. Leisure, *Physica B* **183**, 1 (1993).
6. H. Ogi, K. Takashima, H. Ledbetter, ML Dun, G. Shimoike, M. Hirao, and P. Bowen, *Acta Mater.* **47**, 2787 (1999).
7. H. Ogi, N. Nakamura, K. Sato, M. Hirao, and S. Uda, *IEEE Trans. Ultrason., Ferroelect., Freq. Contr.* **50**, 553 (2003).
8. P. Heyliger, *J. Acoust. Soc. Am.* **107**, 1235 (2000).
9. G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties : A HANDBOOK*, (THE M.I.T. PRESS, 1971).
10. S. Shikata, H. Nakahata, A. Hachigo, and N. Fujimori, *Diamond Relat. Mater.* **2**, 1197 (1993).
11. N. Nakamura, H. Ogi, M. Hirao, N. Tatsumi, T. Imai, and H. Nakahata, *J. Appl. Phys.* **15**, 6405 (2003).