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Citation	Applied Physics Letters. 2005, 86(23), p. 231904-1-231904-3
Version Type	VoR
URL	https://hdl.handle.net/11094/84205
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APPLIED PHYSICS LETTERS **86**, 231904 (2005)

Off-diagonal elastic constant and *sp*^{2}-bonded graphitic grain boundary in nanocrystalline-diamond thin films

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(Received 3 February 2005; accepted 3 May 2005; published online 31 May 2005)

This letter studies the relationship between the off-diagonal elastic constant C_{12} and bond configuration in nanocrystalline-diamond (NCD) thin films deposited by the nitrogen-doped chemical vapor deposition method. The film thickness was varied between 2.4 and 11.3 μm. The elastic constants were measured by resonant-ultrasound spectroscopy coupled with laser-Doppler interferometry. The diagonal elastic constants C_{11} and C_{44}, and Young's modulus in NCD films are smaller than those of the bulk polycrystalline diamond and microcrystalline-diamond (MCD) thin films, and they decrease as the film thickness decreases. However, the off-diagonal elastic constant of the NCD films is significantly larger than that of the bulk diamond, while that of the MCD films is smaller. Micromechanics calculations revealed that this exceptional enhancement of C_{12} occurs when the material includes randomly distributed thin graphitic plates in the isotropic diamond matrix. Thus, this result indicates that the NCD films consist of *sp*^{3}-bonded diamond grains and *sp*^{2}-bonded grain boundaries. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1946920]

Recent developments in the chemical vapor deposition (CVD) technique have made it possible to deposit nanocrystalline diamond (NCD) films on metallic or semiconductor substrates by incorporating nitrogen impurities into the reactant gases.[1–4] NCD films now create an emerging field of study because of their attractive mechanical and electrical properties, such as high hardness, high stiffness, flat surface, and enhanced electrical conductivity.

Microstructure and bond configuration in NCD have been studied by Raman spectroscopy[4–6] and electron energy-loss spectroscopy[3] as well as transmission electron microscopy.[1–4] These intensive studies indicate that in NCD films the grains are composed of *sp*^{3}-bonded carbon atoms with a high degree of short-range ordering and the grain boundaries contain a large fraction of *sp*^{2}-bonded atoms. Because the Raman spectra suggest that *sp*^{2} bonds at grain boundaries are distorted,[4,6] the bond strength between grains will be weak. Thus, the NCD film consists of the tightly bonded atoms in diamond grains and relatively weak intergrain bonds. We here show the relationship between such a specific microstructure of NCD films and the elastic-constant tensor.

The elastic constants of NCD films are of great interest because they determine the geometrical configuration of many surface acoustic wave devices and they are indispensable for evaluating internal thermal stresses. However, the elastic- constant tensor of thin films are not determined accurately by conventional methods such as microtensile tests[7–9] and microbending tests[10,11] because they are highly affected by dimension errors of the specimen and ambiguous gripping condition. We recently developed an alternative method for the determination of anisotropic elastic constants of thin films using free-vibration resonance frequencies of the film/substrate rectangular-parallelepiped specimen:[12–15] Because the resonance frequencies depend on dimensions, mass densities, and all the elastic constants of the film and substrate, measuring them with a sufficient accuracy enables us to determine the elastic constants of the thin film via an inverse calculation. The most important process is the mode identification because mode misidentification yields a physically meaningless answer. We carried out this by measuring the distributions of displacement amplitude on the vibrating specimen using Doppler interferometry and by comparing them with calculations.[16–18]

We prepared five NCD thin films with various film thicknesses between 2.4 and 11.3 μm by the hot-filament CVD method. The substrates were oriented rectangular-parallelepiped monocrystal silicon, measuring $6.0\times4.0\times0.4$ mm^3. Source gases were CH_4, H_2, and N_2, and their flow rates in units of sccm were 6, 200, and 1, respectively. The deposition rate was 0.33 μm/h and substrate's temperature was 620 °C. The pressure during deposition was 50 Torr. The grain size was between 5 and 30 nm. For comparison, we prepared three microcrystalline-diamond (MCD) thin films with thicknesses between 3.8 to 17.3 μm; source gases were CH_4 and H_2, and their flow rate was 3 to 100. Deposition rate was 0.64 μm/h and substrate's temperature was 720 °C. The grain size was of the order of the film thickness. We measured the film thickness and grain size with a field-emission scanning-electron microscope on the cross section. Raman spectroscopy was performed for the NCD and MCD films. The Raman spectra for MCD films showed a high and sharp peak at 1332 cm^{-1}, indicating a

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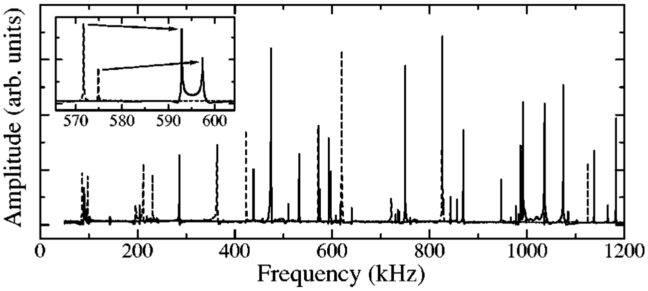


FIG. 1. Resonance spectra of the silicon substrate alone (broken line) and 2.43 μm NCD/Si specimen (solid line).

large volume fraction of the sp^3-bonded region, whereas those of NCD films showed a much lower sp^3-bonded peak and a higher and broader peak centered near 1500 cm^{-1}, indicating a larger volume fraction of the distorted sp^2-bonded region.[4]

We first measured the resonance frequencies of silicon substrate alone and then measured them after the deposition of the diamond films. Figure 1 shows an example of the observed resonant spectra for the silicon substrate and the 2.43 μm NCD/Si specimen. Figure 2 compares the changes of the resonance frequencies caused by the deposition for all specimens with the differences between measured and calculated resonance frequencies. The deposition of the diamond films increased the resonance frequencies by 2%–25%, which is much larger than the calculation error of the resonance frequencies ($\sim$0.2%), ensuring that we obtained reliable sets of elastic constants of the diamond thin films. We estimated possible errors in the resultant elastic constants taking account of two principal error sources: (i) the error in the thickness of the thin film and (ii) errors in the measured resonance frequencies. The former causes errors in the elastic constants of thin films that are nearly proportional to the film-thickness error. The second factor causes different errors in the elastic constants depending on their contributions to the resonant frequencies. Because the off-diagonal elastic constant is less sensitive to resonance frequencies, the error caused by these two factors is larger than those in the diagonal elastic constants. Thus, we determined the possible maximum errors based on the calculation of contributions of individual elastic constants to resonance frequencies. Details are given elsewhere.[14] The error bars are shown in Fig. 3.

For mode identification, the distribution of the vibration amplitude at each resonance frequency was measured and compared with that calculated. They showed excellent agreement, achieving unambiguous mode identification.[13,17] We used 25–30 resonance frequencies to yield the two independent isotropic elastic constants of the diamond films.

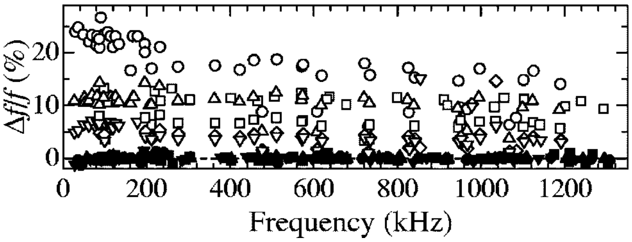


FIG. 2. Normalized changes of resonance frequencies caused by the deposition of diamond films (open marks) and normalized differences between measured and calculated resonance frequencies after the convergence of the inverse calculation (solid marks). Results for all specimens are plotted together.

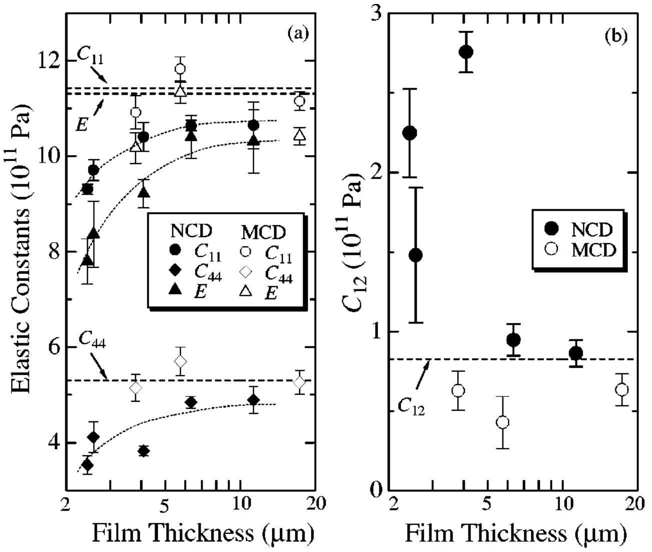
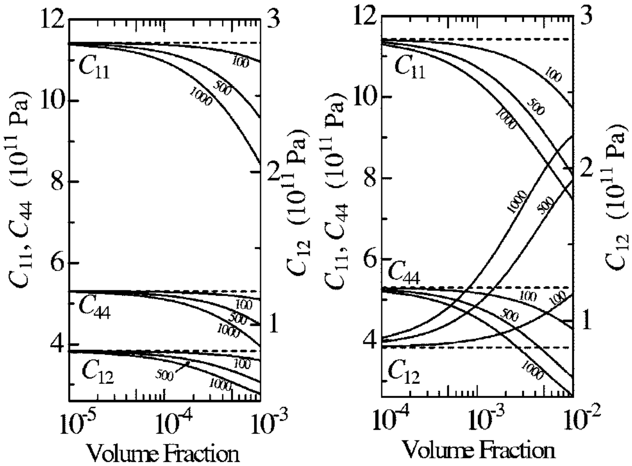


FIG. 3. Thickness dependence of (a) the diagonal elastic constants and Young's modulus and (b) that of the off-diagonal elastic constant. Horizontal broken lines are elastic constants of isotropic bulk diamond.

Figure 3 shows the thickness dependence of the measured elastic constants. Broken lines denote ideal isotropic elastic constants of bulk diamond calculated by the Hill-averaging method.[19] (The Hill-averaging method is not the best averaging method, but it gives good approximation when the material shows a smaller anisotropy factor such as diamond.) Concerning the diagonal elastic-constant components (C_{11} and C_{44}) and Young's modulus [Fig. 3(a)], we find that (i) those of the NCD films are smaller than those of bulk diamond and MCD films and (ii) those of the NCD films depend on the film thickness; thinner NCD films are less stiff. These observations may be attributed to noncohesive bonds between grains; that is, noncohesive bonds on grain boundaries caused softening of polycrystalline materials.[13,20] However, we have to note that the values of C_{12}, the off-diagonal elastic-constant component, of the NCD films are significantly larger than that of bulk diamond and those of the MCD films [Fig. 3(b)]. This observation cannot be explained by the noncohesive bonds at grain boundaries as demonstrated in Fig. 4(a): The macroscopic elastic constants of the polycrystalline diamond including randomly oriented thin pancake-shaped microcracks are calculated by the micromechanics model to simulate the soft regions at grain boundaries. The calculation proceeded in two steps:[20] (i) Calculation of hexagonal elastic constants of such a composite consisting of the isotropic diamond matrix and the thin pancake-shaped inclusions (voids), whose minor axes are oriented along a direction and (ii) calculation of the direction-over-averaged elastic constants of the composite by the Hill- averaging method. Both the diagonal and off-diagonal elastic constants decrease with the increase of the volume fraction of the defect [Fig. 4(a)]. This model explains the decrease of the elastic constants of the MCD films, but it cannot explain the enhanced off-diagonal elastic constant of the NCD films. Thus, we calculated the elastic constants with another model that the sp^3-bonded diamond grains are bonded each other through thin sp^2-bonded graphitic plates, assuming that the c axis of the hexagonal graphite phase is normal to grain boundaries. Using the reported elastic con-



(a) microcrack (b) graphite plate

FIG. 4. Micromechanics calculation of the elastic constants of polycrystalline diamonds including thin pancake-shaped inclusions of (a) microcrack and (b) graphite plate for inclusion aspect ratios of 100, 500, and 1000.

stants of monocrystal graphite[21] ($C_{11}=1060$, $C_{33}=36.5$, $C_{12}=180$, $C_{13}=15$, and $C_{44}=0.3$ GPa), we calculated the macroscopic elastic constants of the polycrystalline diamond including randomly oriented thin graphite plate by the above process. Figure 4(b) shows the dependence of thus calculated elastic constants on the volume fraction of the inclusion. The diagonal elastic constants again decrease with the increase of the volume fraction, but the off-diagonal elastic constant increases. Therefore, the enhanced off-diagonal elastic constant of NCD films indicates the presence of thin graphitic plates between grains, not microcrackings. Many previous studies[2–5] actually showed that grain boundaries of NCD contain larger fraction of the sp^2 bond compared with those of MCD. We here propose a view that the off-diagonal elastic constant can be a characteristic of the sp^2-bonded region at grain boundaries. The thickness dependence of the elastic constants of the NCD film is then interpreted as the increase of the fraction of the sp^2-bonded region as the thickness decreases.

In summary, resonant-ultrasound spectroscopy with the laser-Doppler interferometry determined the independent elastic constants of NCD and MCD thin films, and we found an important relationship between the off-diagonal elastic constant and the sp^2-bonded regions between diamond grains. The diagonal elastic constants and Young's modulus of the NCD films are smaller than those of bulk diamond, but the off-diagonal modulus is much larger. The micromechanics calculation explained this unusual trend by taking account of the microstructure consisting of sp^3-bonded diamond grains and randomly oriented thin pancake-shaped graphitic inclusions. Thus, the off-diagonal elastic constant can be an important characteristic of sp^2-bonded region.

This study was supported by Industrial Technology Research Grant Program in '04 from New Energy and Industrial Technology Development Organization (NEDO) of Japan. A part of this study was conducted as part of the High-Tech Research Center Program and the Center of Excellence (COE) Program, funded by Ministry of Education, Culture, Sports, Science and Technology of Japan.

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