Residual Stress Distribution in the Direction of the Film Normal in Thin Diamond Films

著者	坂　真澄
journal or publication title	Journal of applied physics
volume	86
number	1
page range	224-229
year	1999
URL	http://hdl.handle.net/10097/35466

doi: 10.1063/1.370720

Residual stress distribution in the direction of the film normal in thin diamond films

Shoji Kamiya,[a)] Masaki Sato, and Masumi Saka
Department of Mechanical Engineering, Tohoku University, Aramaki aza Aoba 01, Aoba-ku, Sendai 980-8579, Japan

Hiroyuki Abé
Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

(Received 15 July 1998; accepted for publication 23 March 1999)

The residual stress distribution in the direction of the film normal in thin diamond films deposited on Si substrate has been evaluated together with the distribution of Young's modulus. The films were deposited on the substrate by the microwave chemical vapor deposition method. It has been observed that the curvature of the diamond films delaminated from the Si substrate is functionally dependent on the film thickness. Young's modulus, which has been estimated by the film bending test in conjunction with a finite element method of analysis, appears to be gradually decreasing towards the adhesion interface. On the basis of detailed measurement of curvature and with the aid of Raman spectroscopy, the residual strain distribution in the film has been evaluated. Although the average intrinsic stress was tensile as reported earlier, we have found that a huge compression concentrates in the very small region near the adhesion interface. This finding shows evidence that something happens on the interface, which is absolutely different from the subsequent process of film growth. © *1999 American Institute of Physics.* [S0021-8979(99)01113-5]

I. INTRODUCTION

In recent years, thin solid films are used in many kinds of applications. They are used to constitute integrated circuits on silicon wafers, and also used as the wear protection coatings on cutting tools or hard disks in computers. Thin films are usually deposited on a substrate of different materials. Because the films are very thin, the adhesion interface has a great influence on the state of films. But we hardly know about what happens on the interface when two different materials are connected. It is well known that much residual stress exists in the films, which may cause the failure of protection coatings or undesirable change in semiconductor properties, for example. Therefore, evaluation of residual stress is very important for assessing the integrity of thin solid films in many applications.

Synthetic polycrystalline diamond films produced by chemical vapor deposition (CVD) onto the substrates are recently being used in a variety of applications due to their extreme properties,[1–3] for example, the highest hardness, stiffness, thermal conductivity at room temperature, and also good corrosion resistance. In addition, diamond film is also expected to be used as a new semiconductor material, specially for the high temperature environment.[4] Residual stress in diamond films was evaluated by Rats *et al.*[5] and Chiou *et al.*,[6] where the curvature of films on substrates with known elastic constants was measured. Ager and Drory,[7] Guo and Alam,[8] Yoshikawa *et al.*,[9] Knight and White,[10] and Mohrbacher *et al.*[11] utilized Raman spectroscopy for the evaluation of strain in the diamond crystals of the film. The x-ray diffraction technique is also a popular method to directly measure the lattice strain which was, however, modified for the evaluation of residual stress in thin diamond films by Mohrbacker *et al.*,[11] Choi *et al.*,[12] and Acker *et al.*[13] In these reports, it has been claimed that diamond films have tensile intrinsic stress,[5,8,11,12] which is the residual stress excluding the effect of thermal expansion misfit. However, it is noted that these evaluated values of stress are just the averaged ones over the thickness of films. The distribution of residual stress in the direction of the film normal is still difficult to obtain, since even the x ray has a penetration depth of several microns which is fairly larger than the thickness of thin diamond films.

From a physical point of view, diamond films are indeed not uniform over all the thickness. For example, the grain size in polycrystalline CVD diamond films obviously increases with the distance from the adhesion interface.[14] Baglio *et al.*[15] and Wang *et al.*[16] studied the relation between residual stress and grain size of CVD diamond, where they concluded that residual stress would be severer when grain size decreased. Even in the case of homoepitaxial CVD diamond film growth on natural diamond substrate, Behr *et al.*[17] revealed, by performing micro-Raman spectroscopy on a polished cross section, that the width of the zone-center phonon line increases with the increase of distance from the film/substrate interface. With the aid of transmission electron microscopy, Wang *et al.*[18] observed the characteristics of misfit dislocation on the interface between epitaxially grown CVD diamond and c-BN. All of these reports suggest the considerable gradient of residual stress in the direction of the film normal, and thus the evaluation of average residual stress should not be sufficient to characterize CVD diamond films.

[a)]Electronic mail: kamiya@abe.mech.tohoku.ac.jp

TABLE I. Specimens.

Deposition time (h)	Film thickness t (μm)
2	0.35
3	0.74
5	1.04
7	1.58
10	2.50
17	3.82

Under these circumstances, an attempt is made in the present paper to evaluate the distribution of residual stress in the direction of the film normal in thin diamond films deposited on silicon substrate. Attention is also paid to the distribution of Young's modulus, which must be closely related to the structure of films and may have significant influence on the state of residual stress. Young's modulus of the diamond films has been evaluated also as an averaged one over the film thickness by, e.g., Hollman *et al.*[19] and Chandra and Clyne,[20] but we hardly know about its distribution in the direction of the film normal. When the film is delaminated from the substrate, free standing diamond films appear to have significant curvature that varied interestingly with respect to the film thickness. The distribution of residual stress and Young's modulus has been obtained by solving inverse problems on the basis of the experimentally measured curvature and flexural rigidity of films having different thickness.

II. EXPERIMENTAL OBSERVATION

A. Deposition of diamond films

We used ⟨100⟩ silicon (Si) wafers as the substrate which has a thickness of 0.5 mm. Prior to deposition, the substrates were lightly scratched with the help of 2 μm diamond powder in order to enhance the diamond nucleation, and rinsed in water. Diamond growth was realized in a microwave plasma reactor at the excitation frequency of 2.45 GHz with the gas mixture of 99% hydrogen and 1% methane, and a total gas flow rate of 100 sccm. Substrate temperature was controlled to be 1120 K. In the early stage of deposition, discrete particles of diamond crystal appeared sparsely on the substrate and then grew up in contact with each other to form a continuous film within a period of slightly less than 1 h. We obtained six diamond films with different film thicknesses, by varying the period of deposition, as indicated in Table I. The actual film thickness was measured from the cross sectional observation by a scanning electron microscope (SEM). Figure 1 shows a typical cross section of the diamond film on Si substrate observed by SEM. It should be noted that small disordered diamond crystals can be seen in the neighborhood of adhesion interface; the size of crystals increases gradually with the increase of distance from the interface, and columnar crystals are observed far from the interface.

B. Curvature of free standing films

Deposited films were cut into square flakes along with the substrate by a YAG laser, and then delaminated by etching off the substrate in potassium hydroxide (KOH) solution.

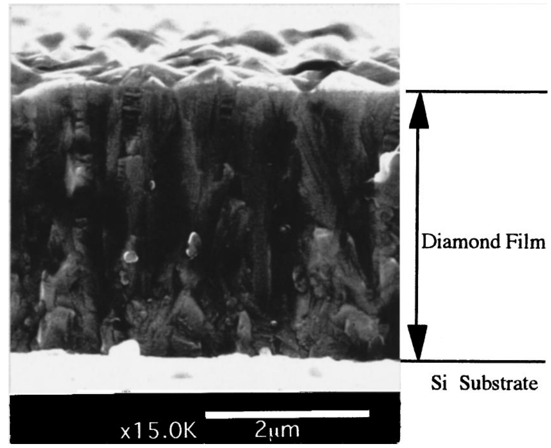

FIG. 1. Cross sectional SEM observation of the diamond film on Si substrate.

These specimens of free standing diamond films appeared to be warped to cylindrical shape[21] when they were delaminated from the substrate, as shown in Fig. 2. Because of this fact, a gradient of residual stress distribution in the direction of the film normal can plausibly be expected. Note that the adhesion interface had been on the convex side of the delaminated films.

Residual stress is usually classified into two categories.[22] One is the thermal stress which is induced during the cooling process from deposition temperature to room temperature, due to the difference of thermal expansion coefficients in the film and substrate. Another is called intrinsic stress, built up during the film growth process itself due to some reasons. When the delaminated film was again heated to the deposition temperature in the CVD reactor, its curvature was observed to be unchanged. Hence the thermal expansion coefficient of the film was constant over the thickness, and warping of the film is expected as a result of intrinsic stress distribution in the direction of the film normal. The gradient of intrinsic stress distribution would be related to the structure of the film as presented in Fig. 1.

In recent studies,[5,8,11,12] intrinsic stress in diamond films is reported to be tensile. Therefore, as we can suppose that intrinsic stress is induced by disordered crystal structure,[12,15,16] it is natural to expect larger tensile stress on the interface side. Also, it should be noted that diamond has a smaller lattice constant than that of silicon, which will lead

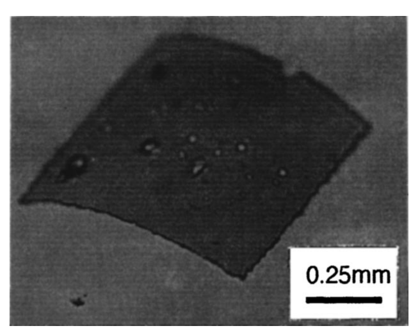

FIG. 2. Typical observation of delaminated film. The adhesion interface is on the convex side of the film.

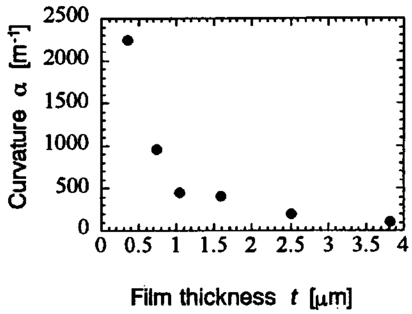

FIG. 3. Relation between thickness and curvature of delaminated films.

to tensile intrinsic stress in the films at the interface. However, it should be remembered again that the interface was on the convex side of the delaminated films. This is an embarrassing contradiction. The curvature of specimens α was measured by using a differential interference microscope and is plotted in Fig. 3 against the film thickness t. Mysteriously enough, the thinner film has outstandingly larger curvature. Figure 3 is likely to suggest an unimaginable distribution of intrinsic stress in the CVD diamond films.

C. Flexural rigidity of free standing films

Bending tests on the free standing film specimens were also carried out, where the specimens were put on a flat base and transversely loaded at the center from the convex side as illustrated schematically in Fig. 4. A linear relationship between the applied load and load point displacement, i.e., the specimen compliance, was obtained for every specimen.

Meanwhile, the deflection of specimens can be numerically calculated as a linear function of applied load by using the finite element method (FEM); the equivalent flexural rigidity[23] of each specimen is evaluated by conforming the same specimen compliance as obtained experimentally. Evaluated flexural rigidity, divided by the cube of film thickness t^3, is plotted against the film thickness in Fig. 5. In the case of the film with uniform distribution of elastic constants, the flexural rigidity should be proportional[23] to t^3 and should appear as a horizontal straight line in Fig. 5. Hence Fig. 5 suggests that the film will be softer on the interface side.

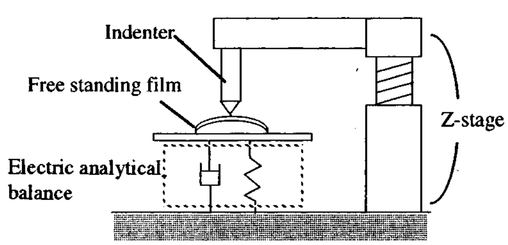

FIG. 4. Schematic illustrations of the bending test on delaminated film specimens.

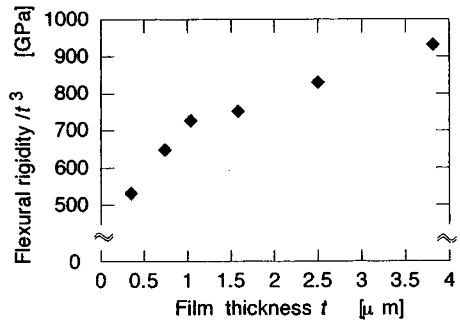

FIG. 5. Flexural rigidity of free standing films.

III. EVALUATION OF YOUNG'S MODULUS AND RESIDUAL STRESS

A. Distribution of Young's modulus

Since deformation of the film, when delaminated from the substrate, is controlled simultaneously by both the residual stress and elastic constants, first we evaluate the distribution of Young's modulus in the direction of the film normal by solving an inverse problem.

Now let us focus again on the cross sectional crystal structure of the diamond film, where the size of crystal grains changes along with the distance from the adhesion interface (see Fig. 1). Observation made on the films having different thickness reveals that the crystal grain size seems to be determined by the absolute distance from the interface, but not by the position relative to the entire film thickness. In other words, the distribution of crystal grain size in the direction of the film normal seems to be identical, which is common for all the specimens and independent of the film thickness. This fact might suggest that the crystal structure constituted earlier will not be changed by the subsequent piling up of crystals. As Young's modulus is supposed to vary with the structure of film, its distribution is also regarded as a function of the distance from the interface. Here the z axis is introduced as the coordinate parallel to the film normal with its origin at the interface. According to the monotonic increase of crystal grain size, the distribution of Young's modulus $E(z)$ is assumed as in the following equation:

$$E(z)=a\exp(bz)+c, \tag{1}$$

where a, b and c are unknown constants to be determined. Having assumed the distribution of Young's modulus, the flexural rigidity D of the film with an arbitrary thickness t can be calculated[23] as

$$D=\frac{1}{1-\nu^2}\int_0^t (z-m)^2 E\,dz, \tag{2}$$

where it was mentioned that another elastic constant, Poisson's ratio ν, is supposed to be 0.07[7,24] throughout our calculation. In Eq. (2), m represents the position of neutral surface which undergoes no extension nor contraction as a result of bending, and it can be determined by the following:

$$m=\frac{\int_0^t zE\,dz}{\int_0^t E\,dz}. \tag{3}$$

Since the actual values of flexural rigidity D have already been obtained experimentally for all the specimens, as presented in Fig. 5, the optimum values of unknown constants a, b and c in Eq. (1) can be determined by minimizing the difference between the measured and calculated flexural rigidity for all the specimens, in the sum-square sense.

B. Distribution of residual stress

Once the distribution of Young's modulus can be obtained, we can evaluate the distribution of residual stress in connection to the variation of curvature presented in Fig. 3. Since the curvature of the film adhered to the substrate is almost zero at room temperature, the total strain ϵ in the film can be assumed to be zero over the thickness when adhered to the substrate. Then, the biaxial residual stress, σ, in the film can be expressed by the following equations:

$$\sigma=\frac{E}{1-\nu}\varepsilon_e, \tag{4}$$

$$\varepsilon=\varepsilon_e+\varepsilon_i=0, \tag{5}$$

where ϵ_e and ϵ_i are elastic and inelastic strain, respectively. According to the cross sectional crystal structure of the film, we assume the distribution of inelastic strain again as in the case of Young's modulus,

$$\varepsilon_i(z)=f\exp(gz)+h, \tag{6}$$

where f, g and h are unknown constants to be determined. For the case of delaminated free standing film with a curvature of α in one direction (x direction), the total strain is considered according to Kirchhoff's hypothesis as follows:

$$\begin{aligned}\varepsilon_x'&=\alpha(z-m)+\beta=\varepsilon_{ex}'+\varepsilon_i,\\ \varepsilon_y'&=\beta=\varepsilon_{ey}'+\varepsilon_i.\end{aligned} \tag{7}$$

In Eq. (7), ϵ_x' and ϵ_y' represent the total strain in two orthogonal directions, x and y, and ϵ_{ex}' and ϵ_{ey}' represent their elastic components. In addition, β is the strain of neutral surface, which is situated at $z=m$ and undergoes no extension nor contraction during the process of bending. Note that β can be measured as the average of residual stress variation between prior and after the delamination by Raman spectroscopy.[7] Also, the curvature α has already been measured as stated in Sec. II. Now, as the left hand side of Eq. (7) is known, the distribution of elastic strain, ϵ_{ex}' and ϵ_{ey}', can be obtained by substituting the inelastic strain ϵ_i assumed in Eq. (6) into the right hand side of Eq. (7), since the inelastic strain should not change during the process of delamination. Then, the state of stress in free standing film can be described as follows:

$$\begin{pmatrix}\sigma'_x\\ \sigma'_y\end{pmatrix}=\begin{pmatrix}\dfrac{E}{1-\nu^2} & \dfrac{\nu E}{1-\nu^2}\\ \dfrac{\nu E}{1-\nu^2} & \dfrac{E}{1-\nu^2}\end{pmatrix}\begin{pmatrix}\varepsilon_{ex}'\\ \varepsilon_{ey}'\end{pmatrix}. \tag{8}$$

Because the delaminated film is free from any external force, the stress must satisfy the equilibrium of membrane force and moment integrated over the thickness. By minimizing the residual sum of squares of equilibrium for all six specimens, the distribution of inelastic strain is obtained with the optimum values of f, g and h in Eq. (6). Finally, by substituting the inelastic strain given by Eq. (6) into Eq. (5), the distribution of residual stress in the films on the substrate can be evaluated through the elastic strain in Eq. (5).

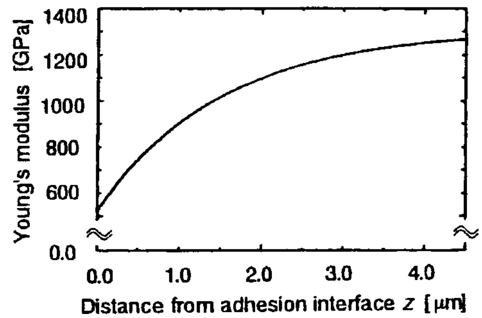

FIG. 6. Evaluated Young's modulus distribution in the direction of the film normal.

IV. RESULTS AND DISCUSSION

Figure 6 shows the evaluated distribution of Young's modulus, where we can see that Young's modulus tends to be smaller as we approach the interface. Since small disordered diamond crystals exist in the region near the interface as shown before in Fig. 1, it is natural that the diamond film is softer on the interface side. Note that the curve is getting closer to the modulus of bulk diamond,[24] away from the interface, while it is almost half of that for bulk diamond just on the interface.

Figure 7 shows the evaluated distribution of residual elastic strain in the film when adhered to the substrate. As shown in Fig. 7(a), nothing special can be seen, rather almost constant distribution of compressive strain is observed over the entire range of film thickness. However, an extremely large compressive strain is observed to be concentrated near the adhesion interface when the figure is magnified [see Fig. 7(b)].

The residual stress σ, calculated by Young's modulus and elastic strain obtained above, is presented by the solid curve in Fig. 8, where the horizontal axis is magnified in the region just near the interface. Then we extract the intrinsic stress σ_{int} as presented by the dotted curve in Fig. 8, by removing the component of thermal stress which is simply calculated from the difference of thermal expansion coefficients[25] between diamond and silicon, since the thermal expansion coefficient of the film is expected to be constant over the thickness as mentioned before. Intrinsic stress in the film is observed in Fig. 8 to be tensile when averaged over the entire thickness, as reported in the earlier studies.[5,8,11,12] However, we can now see the huge compressive stress concentrated near the adhesion interface. This fact might suggest that the structure of interface would be quite different from the other part of the film.

Recently, Chiristiansen *et al.*[26] reported that carbon atoms are driven into the Si substrate during the initial stages of the deposition of amorphous diamond-like carbon films. The surface of the Si substrate is therefore expected to be highly strained due to the implanted carbon atoms which

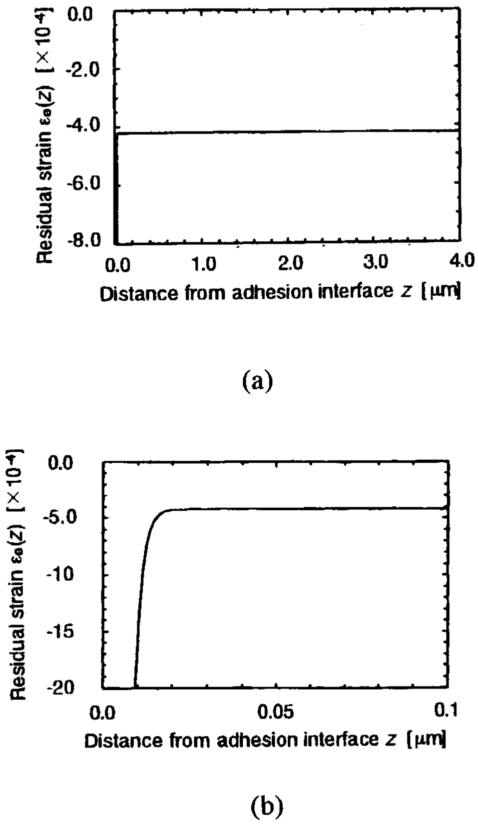

FIG. 7. Evaluated distribution of residual elastic strain in the film when adhered to the substrate.

may form diamond nuclei on condensation in the silicon lattice. Then it is easily imagined that the carbon atoms must be bonded to the overcrowded silicon and implanted carbon atoms to form diamond crystals on the substrate surface, which would naturally result in a large compressive strain in the films just on the interface. Taking into account both their observations[26] and our results presented here, it can be suggested that diamond films and substrates may be essentially strained in compression on both surfaces associated with the interface due to the physical mechanism of diamond nucleation.

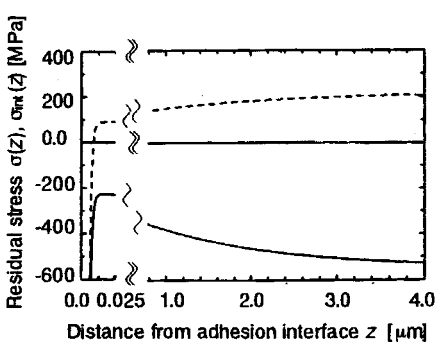

FIG. 8. Evaluated residual stress distribution in the film when adhered to the substrate. The residual stress σ, calculated by Young's modulus and elastic strain in Fig. 7, is presented by the solid curve. Also, intrinsic stress $\sigma_{\rm int}$ is presented by the dotted curve.

V. CONCLUSIONS

The residual stress distribution in the direction of the film normal in thin CVD diamond films deposited on the Si substrate has been evaluated, together with the distribution of Young's modulus. The Young's modulus is observed to take a smaller value near the interface, while it approaches closer to the modulus of bulk diamond away from the interface. The existence of the tensile intrinsic stress, as reported in earlier studies, has also conformed in our present study to an averaged one over the entire thickness. However, it is found that huge compressive stress concentrates near the adhesion interface. No other methods such as x-ray diffraction or Raman spectroscopy will be able to detect such a stress distribution in the extremely thin region near the interface. Unfortunately we still do not understand all of the phenomena which happen on the interface for the connection of two different materials. However, here we have found mechanical evidence that something quite different from the rest of the film growing process is happening near the interface at the very early stage of deposition, where the region of interest is even far thinner than the thickness of thin films.

ACKNOWLEDGMENTS

This work was partly supported by Grant-in-Aid for Scientific Research (B)(2) Nos. 08455050 and 10555024, and Grant-in-Aid for Encouragement of Young Scientists (A) No. 09750094 from the Ministry of Education, Science, Sports and Culture of Japan. The authors also wish to thank Associate Professor H. Yugami, Tohoku University, for his help in measurement of residual stress by Raman spectroscopy, and Dr. S. Reaz Ahmed for his advice on improving the manuscript. A part of this work was performed at Venture Business Laboratory at Tohoku University.

[1] W. A. Yarbrough and R. Messier, Science **247**, 688 (1990).
[2] J. C. Angus and C. C. Hayman, Science **241**, 913 (1988).
[3] K. E. Spear, J. Am. Ceram. Soc. **72**, 171 (1989).
[4] W. P. Kang, J. L. Davidson, Y. Gurbuz, and D. V. Kerns, J. Appl. Phys. **78**, 1101 (1995).
[5] D. Rats, L. Bimbault, L. Vandenbulcke, R. Herbin, and K. F. Badawi, J. Appl. Phys. **78**, 4994 (1995).
[6] Y. H. Chiou, C. T. Hwang, M. Y. Han, J. H. Jou, Y. S. Chang, and H. C. Shih, Thin Solid Films **253**, 119 (1994).
[7] J. W. Ager and M. D. Drory, Phys. Rev. B **48**, 2601 (1993).
[8] H. Guo and M. Alam, Thin Solid Films **212**, 173 (1992).
[9] M. Yoshikawa, Y. Mori, M. Maegawa, G. Kitagiri, H. Ishida, and A. Ishitani, Appl. Phys. Lett. **55**, 2608 (1989).
[10] D. S. Knight and W. B. White, J. Mater. Res. **4**, 385 (1989).
[11] H. Mohrbacher, K. Van Acker, B. Blanpain, P. Van Houtte, and J. P. Celis, J. Mater. Res. **11**, 1776 (1996).
[12] S. K. Choi, D. Y. Jung, and H. M. Choi, J. Vac. Sci. Technol. A **14**, 165 (1996).
[13] K. Van Acker, L. De Buyser, J. P. Celis, and P. Van Houtte, J. Appl. Crystallogr. **27**, 56 (1994).
[14] C. Wild, N. Herres, and P. Koidl, J. Appl. Phys. **68**, 973 (1990).
[15] J. A. Baglio, B. C. Farmsworth, S. Hankin, G. Hamill, and D. O'Neil, Thin Solid Films **212**, 180 (1992).
[16] W. Wang, K. Liao, J. Gao, and A. Liu, Thin Solid Films **215**, 174 (1992).
[17] D. Behr, J. Wagner, C. Wild, and P. Koidl, Appl. Phys. Lett. **63**, 3005 (1993).
[18] L. Wang, P. Pirouz, A. Argoitia, S. M. Jing, and J. C. Angus, Appl. Phys. Lett. **63**, 1336 (1993).

[19] P. Hollman, A. Alahelisten, M. Olsson, and S. Hogmark, Thin Solid Films **270**, 137 (1995).
[20] L. Chandra and T. W. Clyne, J. Mater. Sci. Lett. **12**, 191 (1993).
[21] M. W. Hyer, J. Compos. Mater. **15**, 175 (1981).
[22] F. M. d'Heurle and J. M. E. Harper, Thin Solid Films **171**, 81 (1989).
[23] S. Timoshenko and S. Woinowsky-Krieger, *Theory of Plates and Shells* (McGraw–Hill, New York, 1959).
[24] M. H. Grimsditch and A. K. Ramadas, Phys. Rev. B **11**, 3139 (1975).
[25] G. A. Slack and S. F. Bartram, J. Appl. Phys. **46**, 89 (1975).
[26] S. Christiansen, M. Albrecht, G. Frank, H. P. Strunk, C. Ronning, H. Hofsäss, and E. Recknagel, Diamond Relat. Mater. **7**, 15 (1998).