Tetrahedral amorphous carbon films prepared by magnetron sputtering and dc ion plating

J. Schwan, S. Ulrich, H. Roth, and H. Ehrhardt

Universität Kaiserslautern, FB Physik, Schrödingerstrasse, D-67663 Kaiserslautern, Germany

S. R. P. Silva and J. Robertson

Engineering Department, Cambridge University, Trumpington Street, Cambridge CB2 1PZ, United Kingdom

R. Samlenski and R. Brenn

Universität Freiburg, Fakultät für Physik, Hermann Herderstrasse 3, 79104 Freiburg, Germany

(Received 9 June 1995; accepted for publication 17 October 1995)

Highly tetrahedral, dense amorphous carbon (ta-C) films have been deposited using rf sputtering of graphite by an unbalanced magnetron with intense dc Ar-ion plating at low temperatures ($<70^\circ\text{C}$). The ratio of the argon ion flux to neutral carbon flux Φ_i/Φ_n is about 5. The film density and compressive stress are found to pass through a maximum of 2.7 g/cm^3 and 16 GPa, respectively, at an ion plating energy of about 100 eV. Experiments with higher ion flux ratios of $\Phi_i/\Phi_n=10$ show that it is possible to deposit carbon films with densities up to 3.1 g/cm^3 and sp^3 contents up to 87%. Deposition of ta-C in this experiment when the energetic species is Ar appears to require a minimum stress of 14 GPa to create significant sp^3 bonding, which contrasts with the continuous increase in sp^3 content with stress when the energetic species is C ions themselves. These results are used to discuss possible deposition mechanisms. © 1996 American Institute of Physics. [S0021-8979(96)01603-0]

I. INTRODUCTION

There has been considerable interest in highly sp^3 bonded, tetrahedral forms of amorphous carbon (ta-C) in recent years due to their remarkable physical properties.¹ Koskinen,² and Ishikawa, Ogawa, and Takagi,³ and Lifshitz *et al.*^{4,5} have produced ta-C films containing high fractions of sp^3 bonding using the mass selected ion-beam (MSIB) deposition method. McKenzie, Muller, and Pailthorpe⁶ and Fallon *et al.*⁷ have also produced highly sp^3 bonded ta-C films using a plasma beam of C^+ ions from a filtered cathodic vacuum arc (FCVA). It was found that the properties of ta-C such as density pass through a maximum as a function of C^+ ion energy in each process.

The formation of ta-C by MSIB and FCVA has generally been attributed to deposition by an energetic species, C^+ . It is also possible to produce high-density a-C films by other deposition methods using energetic species,⁸ such as ion-assisted deposition in which energetic Ar ions bombard thermal C atoms during the deposition process. Savvides⁹ was able to produce diamondlike carbon by this method using an unbalanced magnetron, although his method of optical analysis is believed to overestimate the sp^3 content. Cuomo *et al.*¹⁰ were able to prepare a-C films with densities up to 3 g/cm^3 by dual-ion-beam sputtering onto well-cooled substrates. Andre, Rossi, and Dunlop¹¹ prepared diamondlike carbon films with densities up to 2.7 g/cm^3 using a dual-ion-beam system (DIBS) and ion-beam-assisted dc magnetron (IBAM). Kleber *et al.*¹² deposited a-C by magnetron sputtering but the films had a density of 2.0 g/cm^3 , which is typical of many magnetron sputtered films.

This article demonstrates that it is possible to deposit ta-C without the use of C^+ ion beams or plasma beams by using magnetron sputtering in the presence of ion plating (MS/IP). A dc-biased, unbalanced rf magnetron sputter

source is operated under conditions of intense Ar-ion plating. The advantage of the magnetron sputter source is that this technique is widely established in industry and allows the deposition onto large areas with relatively high deposition rates. The use of a suitable unbalanced magnetic-field configuration places the substrate immersed in the plasma so that the growing film is bombarded by energetic Ar ions from the plasma. This MS/IP technique is quite effective and has been used by Ulrich *et al.*¹³ to deposit pure c-BN films.

The a-C films produced by MS/IP are characterized in terms of their density, sp^3 fraction, and intrinsic stress. The article also discusses possible mechanisms for the deposition of ta-C by ion plating. The data show that the deposition mechanism differs from that when the film grows from energetic C^+ ions. The growth of ta-C from energetic C^+ ions is generally believed to be described by the subplantation mechanism in which the C ions are energetic enough to enter subsurface atomic sites. In MS/IP, the energetic species is the Ar^+ ion, which acts only to bombard the growing a-C film and is not incorporated in the film. Three types of deposition processes may be of importance:

- (i) displacement of C atoms by Ar^+ ions into subsurface positions (knock-on or indirect subplantation);
- (ii) surface densification of the sputtered carbon atoms in the thin film by argon-ion bombardment;
- (iii) conversion of sp^2 to sp^3 sites by a high local stress, which is generated by the intense argon ion plating.

These three mechanisms are expected to have different process parameters. The subplantation definitely has a threshold energy, namely the displacement energy, which for carbon lies between 25 and 35 eV. The densification process should be of importance at low collision energies (few eV) and high ion flux rates Φ_i (compared to the flux rate of

neutral carbon atoms Φ_n). The stress-induced phase transition in the pT phase diagram must show a stress threshold.

II. EXPERIMENT

The magnetron is described in detail elsewhere.^{14,15} In an unbalanced magnetron, the plasma extends over both the target and the substrate, so that the Ar ions provide both the sputtering flux to the graphite target and the ion plating flux on the growing film. A high flux of neutral C atoms is achieved by placing the magnets as close as possible to the graphite target. The configuration of the magnets is a critical parameter, as this determines both the neutral carbon flux Φ_n and the Ar-ion flux Φ_i , thereby controlling the deposition rate and the ion plating intensity.

The substrates are sputter cleaned before deposition for 15 min and they are placed at a distance of 60 mm from the target. All films have been deposited with rf power of 200 W and rf frequency of 13.56 MHz. The argon pressure is kept constant at 1.4×10^{-3} mbar. The substrate temperature remains below 70 °C. The ion energy and ion fluxes are determined by a Faraday cup placed at the substrate position using a retarding field.

The density and sp^3 content were measured by electron-energy-loss spectroscopy (EELS). The plasmon spectra of the films were recorded on a 25 keV electron loss spectrometer with a typical energy resolution of 0.38 eV and an acceptance angle of 2 mrad. The spectra were corrected for the effects of multiple inelastic scattering and of the restricted acceptance angle. The density was deduced from the valence plasmon energy. Further EELS measurements were performed using a Philips CM30 transmission electron microscope (TEM) operated at 100 keV. The sp^3 content was derived from the intensity of the π^* peak in the C K loss spectrum, measured on a dedicated parallel EELS spectrometer on a TEM.

The stress was derived from the curvature of the Si substrates using Stoney's equation. The thickness of the films is about 100 nm measured by ellipsometer and profilometer. The argon content was measured by Rutherford backscattering with He^+ ion energy of 2 MeV.

Films for optical gap measurements were prepared on quartz glass substrates, and the bias voltage was applied in the form of a rf self-bias. The Tauc gap was determined from transmission and reflection spectra.

III. RESULTS AND DISCUSSION

A. Film properties

The analysis of the ion energy distribution and ion mass spectra show that the flux at the substrate consists mainly of neutral C atoms and Ar^+ ions.¹⁴ The mass analysis shows that the C ion flux is only about 1% of the C atom flux and therefore it does not play a significant role in the deposition process.

The energy E_n of the neutral C atoms results from the energy distribution of the sputter process and amounts to a few eV.¹⁵ The energy of the Ar ions for zero bias voltage is given by the plasma potential of 24.2 eV and it has a rather sharp energy distribution of 7 eV. With additional bias the

FIG. 1. Stress as a function of argon-ion plating energy for carbon films deposited at a Φ_i/Φ_n ratio of 5.4.

width of the energy distribution remains constant. The ratio Φ of the argon ion flux Φ_i to carbon neutral flux Φ_n is found to be 5.4. This means that on average each carbon atom is hit by about five argon ions while it rests on the film surface. The product $E_n\Phi_n$ is much smaller than $E_i\Phi_i$ of the argon ions and can be neglected in the energy balance during film formation.

The C atom flux was derived from the mass deposition rate. The deposition rate is 0.43 Å/s at an argon-ion energy of 24.2 eV and decreases to 0.27 Å/s for an Ar-ion energy of 130 eV. Since Φ_n and E_n remains constant, the reduction in film thickness with increasing ion plating energy results partly from the densification of the material and partly from resputtering of the deposited carbon film.

Figure 1 shows the variation of the intrinsic stress of the α -C films as a function of Ar^+ -ion energy for an ion flux ratio of $\Phi=5.4$. For each Ar plating energy the stress has been measured for five times always showing the same behavior. Here the medium stress of those measurements is plotted in Fig. 1. The stress is compressive, and it is intrinsic because the films are deposited at room temperature, so there is no component due to the thermal expansion coefficients. The stress is seen to increase gradually and to pass through a maximum of 16 GPa at an Ar^+ energy of 100 eV before decreasing again at higher Ar^+ energies. The compressive stress variation is found to be more sharply peaked at a flux Φ of 10, reaching a value of 19 GPa at a slightly lower Ar-ion energy of 90 eV.

Figures 2 and 3 show the variation of the density and sp^3 content with Ar^+ energy for $\Phi=5.4$ and 10. As the Ar^+ energy increases, the density is seen to remain at a graphitic value of about 2.0 g/cm³ up to 70 eV and then to increase sharply to a peak of 2.7 g/cm³ at around 105 eV for $\Phi=5.4$ and to a peak of 3.1 g/cm³ at 90 eV for $\Phi=10$. The density then decreases sharply at highly Ar^+ energies to its graphitic value. The sp^3 fraction behaves roughly in a similar fashion, staying at quite low sp^3 values and then increasing sharply for Ar^+ energies around 80–120 eV, before decreasing

FIG. 2. Density as a function of argon-ion plating energy for films deposited at $\Phi=5.4$ (solid symbols) and $\Phi=10$ (open symbols). Films deposited at the different Φ ratios were analyzed by EELS electron beams with beam characteristics (●) 25 keV and 2 mrad and (■) 100 keV and 10 mrad.

sharply again. The peak value of sp^3 fraction is 60% for $\Phi=5.4$ and 87% for $\Phi=10$.

In order to gain more information about the deposition mechanism, it is instructive to plot the density and sp^3 fraction against compressive stress, as shown in Figs. 4 and 5. The density variation is seen to lie on the same curve plotted versus stress for both ion flux ratios. The density is seen to remain low until the stress reaches about 13 GPa, and then increases strongly with stress. The sp^3 fraction also varies in a similar fashion with stress, remaining relatively constant and then increasing rapidly once the stress exceeds the threshold of 13 GPa. There is a greater scatter for the sp^3 data; the sp^3 values at low stress appear slightly higher for $\Phi=10$, but the data tend to lie in the same curve above the threshold.

This variation of density and sp^3 content with stress is different from that found in ta-C deposited from the FCVA,

FIG. 4. Density vs stress for carbon films deposited at (●) $\Phi=5.4$ (25 keV, 2 mrad); (○) $\Phi=5.4$ (25 keV, 2 mrad); (□) $\Phi=10$ (100 keV, 10 mrad).

where the films are deposited by energetic C^+ ions themselves, where they are found to vary essentially linearly with stress.^{6,16}

Figure 6 shows that the sp^3 content varies linearly with density. A similar variation was found for ta-C from the FCVA.^{6,16} A similar dependence is found because the dependence of density on sp^3 content is essentially a property of the material.¹⁶ In contrast, the dependence of density and sp^3 content on stress is a function of the deposition process itself.

Figure 7 shows the Ar content of the a-C films as a function of Ar^+ energy as determined by Rutherford backscattering spectroscopy (RBS). The Ar content is seen to be quite low, 6%, and to decrease to a value of only 3% at an Ar^+ energy of 100 eV, where the film density reaches a maximum. This suggests that Ar incorporation is restricted when the ta-C density is high. Further this suggests that the main component of the stress must come from the carbon structure itself.

FIG. 3. sp^3 content as a function of argon-ion plating energy for (■) $\Phi=5.4$ and (□) $\Phi=10$.

FIG. 5. sp^3 content vs stress for carbon films deposited at (■) $\Phi=5.4$ (100 keV, 10 mrad) and (□) $\Phi=10$ (100 keV, 10 mrad).

FIG. 6. Density vs sp^3 content for carbon films deposited at (■) $\Phi=5.4$ and (□) $\Phi=10$.

B. Deposition mechanism

The creation of sp^3 sites in ta-C prepared by energetic C^+ ion deposition is generally believed to arise from subplantation.^{4,17}

The ion has sufficient energy to penetrate the surface atomic layer and enter a subsurface atomic site. There are two ways a C atom could occupy a subsurface site, either by direct penetration [Fig. 8(a)] or by incident ion displacing a surface atom into that site [Fig. 8(b)]. The subplantation also creates a large compressive stress. This process has been analyzed recently,^{17,18} and analytic expressions have been given for the fraction of sp^3 sites.

MS/IP deposition differs in that energetic Ar^+ ions can only displace C atoms from the surface into subsurface sites. This is analogous to the displacement process in Fig. 8(b). Subplantation by both process (a) and (b) requires the ion energy to exceed a threshold, close to the displacement energy of about 25 eV.¹⁷ The density should then increase gradually above this energy, until it begins to decrease at high ion energies, due to the annealing in a thermal spike.

FIG. 7. Argon content as a function of argon-ion plating energy.

FIG. 8. Direct and knock-on (indirect) penetration by ions.

The density and sp^3 content clearly do not follow this behavior in the MS/IP ta-C. This suggests that the knock-on subplantation, process (b), is not particularly efficient, in that there is little increase in density up to say 60 eV. In contrast the compressive stress is found to follow the expected dependence on ion energy. However, this is still not consistent with the original subplantation model in that the stress and density should correlate with each other.

A second possible process is that the Ar -ion bombardment could cause a densification of surface layers by displacing C atoms inward. In this model the densification and stress formation of the sputtered carbon atoms in the films are due to energy and momentum transfer by low-energy argon-ion plating. The knock-on collisions of the argon ions ensures that void formation is unlikely. This process is expected to be significant because each C atom is hit by on average five Ar^+ ions before being covered by the next layer. Densification differs from subplantation in that it does not require a threshold energy. The lack of densification at low energies however suggests that this process is relatively small in MS/IP.

The third possible process is a stress-induced transformation of sp^2 sites to sp^3 sites. McKenzie and co-workers⁶ attributed the generation of ta-C to a quasithermodynamic transition on a pressure/temperature phase diagram. In his model, pressure is generated by the stress in the films whereas temperature is generated by energetic carbon ions impinging on the surface of the carbon film. Takano, Harashima, and Wakatsuki,¹⁹ Endo *et al.*,²⁰ and Yagi *et al.*²¹ have shock compressed graphite at room temperature. They reported a martensitic (displacive) phase transformation from sp^2 to sp^3 bonded carbon at room temperature for pressure values above 15 GPa. Scandolo *et al.*²² and Kitabatake²³ showed by *ab initio* molecular-dynamic studies a pressure-induced transformation path of graphite to diamond. In the case of MS/IP ta-C we observe that the deposition process has created a very large compressive stress. This stress is larger than that found in ta-C formed by FCVA. Simulations suggest that the stress is not uniform but varies between sites.²⁴ Since the sp^3 content enhances rapidly if the stress exceeds values above 14 GPa (see also Fig. 7), we propose

FIG. 9. Spin density as a function of argon-ion plating energy.

that this stress causes pairs of sp^2 sites to bond together to form sp^3 sites. The stress in the films induces a phase transformation of sp^2 to sp^3 hybridized carbon. The observed threshold stress is large, about 14 GPa from Figs. 4 and 5. This stress is much larger than that given by the Berman–Simon line 1.6 GPa, which corresponds to the isothermal conversion of graphite to diamond. It seems that stress values above say 4 GPa and below 14 GPa are a necessary condition for the preparation of ta-C films, but they are not a sufficient condition for the preparation of ta-C films.

The different processes can clearly be distinguished by their different threshold energies. In the subplantation model the energy threshold is given by the displacement energy. Densification should occur if ions have a higher energy than the displacement energy. In contrast, there is no threshold in the densification model. The densification by these deposition processes plays a minor role because stress and densification do not correlate with each other and no densification is observed for Ar-ion energies below 60 eV.

In the third process, a threshold stress of about 14 GPa exists for the transformation of sp^2 sites to sp^3 sites. This is close to the threshold observed for shock-compressed graphite.^{19–21}

C. Electrical properties

The Tauc gap of each of the films was found to be low, well below 1 eV, even in those films containing large sp^3 contents. The optical gap is controlled by the configuration of the π states.²⁵ The intense ion bombardment during deposition is likely to produce strong disordering of the sp^2 sites, and to lower the optical gap.²⁶ The lowering of the optical band gap arises from the mixing of σ and π states.

The density of electronically active defect states can be measured by electron-spin resonance (ESR). Figure 9 shows that the spin density is sizeable in MS/IP a -C. The spin density is seen to be a minimum at the Ar^+ energy of maximum density. The spin density is found to be less than in ta-C prepared by the FCVA,²⁷ despite the higher disorder in the present films. This suggests that defect density is not just controlled by the intrinsic disorder.

FIG. 10. Raman spectrum of a MS/IP carbon film deposited at an argon plating energy of 110 eV.

The width of the ESR line gives information on the nature of the defect state. With ESR a narrow ESR line of about 2.5 G is found for films deposited at all argon plating energies. In a -C the spin signal is thought to arise from unsaturated π bonds. A narrow ESR line in a -C is a strong indication that exchange narrowing occurs. A small linewidth of 2.5 G indicates that the π -spin centers are close together and interact, so that those sp^2 clusters where the spins are located are not independent from each other and pairing of spins is likely to occur.

The MS/IP a -C films show a high electrical conductivity ($>4 \Omega^{-1} \text{ cm}^{-1}$). This finding can be understood if we assume connected sp^2 regions. This would also be consistent with the narrow optical gap in these materials. Rossnagel, Russak, and Cuomo²⁸ found that magnetron-sputtered a -C at a pressure of 10^{-3} mbar had a conductivity of $1 \Omega^{-1} \text{ cm}^{-1}$, similar to the value found here. The electronic properties are determined by the sp^2 matrix due to the π - π^* states being closer to the Fermi level.²⁵

D. Raman

The Raman spectrum of the ta-C film for $\Phi=5.4$ is shown in Fig. 10. Generally speaking, the Raman spectra of nanocrystalline C are dominated by the features of the sp^2 component because of its much larger Raman scattering. The Raman spectra are fitted by four Gaussians. The 1600 cm^{-1} G peak corresponds to the zone center Raman mode of graphite. The 1380 cm^{-1} D peak corresponds to the zone boundary mode of graphite which becomes active for finite crystallites.²⁹ The origin of the peak at 1480 cm^{-1} is not clear.

The peak at 1170 cm^{-1} is not due to a sp^2 feature. Nemanich *et al.*³⁰ said that this feature is present in films with small amounts of diamond crystalline domains indicating that it could be a diamond precursor structure. They further suggested that Raman peaks around 1175 cm^{-1} are due to regions of microcrystalline diamond or amorphous diamond. Silva *et al.*³¹ attributed this peak to hexagonal diamond crys-

FIG. 11. Atomic force microscopy picture of a MS/IP ta-C film (deposited at 110 eV argon plating energy) after diamond nucleation of 30 min.

tallites within an amorphous carbon matrix. Wagner, Wild, and Koidl³² attributed the 1150 cm^{-1} peak to nanocrystalline diamond.

The MS/IP deposited films have been exposed to a microwave plasma in a $\text{H}_2(99\%)/\text{CH}_4(1\%)$ mixture, at a substrate temperature 800°C . These conditions are normally suitable for diamond deposition. The atomic hydrogen in the plasma causes preferential etching of amorphous and graphitic carbon structures. These conditions will even etch ta-C which has been deposited by FCVA or by a plasma beam source.³³ However, the plasma does not fully etch ta-C deposited by MS/IP. This indicates that the MS/IP deposited films contains sp^3 nuclei which were not completely etched by atomic hydrogen. The treatment of such films under diamond growing conditions leads to a cauliflower appearance of growth (Fig. 11). Conclusive x-ray diffraction (XRD) measurements for the existence of diamond seeds in the films could not be performed, because the needed film thickness (for XRD) of the carbon films is limited due to the high stress. Synchrotron XRD measurements which can deal with 100-nm-thick films are in preparation.

Therefore we assume that the structure of the MS/IP deposited carbon films is given by a sp^2 matrix or net, in which sp^3 clusters are embedded. It seems that there is some, not yet identified, order in the sp^3 clusters as indicated from Raman spectra and from the diamond nucleation experiment. Such a cluster structure would explain the electronic properties (sp^2 matrix/net) and the high density. Also stress and sp^3 content are explained by the existence of such clusters.

The physical properties of the ta-C films prepared under the MS/IP conditions are completely different to those of the ta-C prepared by the MSIB technique or vacuum arc. Table I shows some physical properties for ta-C prepared by the indirect subplantation process (MS/IP) and direct subplantation process (FCVA). The different physical properties of the ta-C films have their origin in the different microstructures of the materials.

TABLE I. Physical properties of ta-C films prepared by the MS/IP technique and FCVA (Refs. 6, 7, and 35).

	MS/IP	FCVA
sp^3 content	87%	<90% ^a
Density	3.1 g/cm^3	$\approx 3.1\text{ g/cm}^3$ ^b
Stress	<19 GPa	<11 GPa ^c
Optical gap	$\approx 0\text{ eV}$	$1.5\text{--}2.1\text{ eV}^c$
Electrical resistance	at $\Phi_i/\Phi_n=5$ <0.25 $\Omega\text{ cm}$ at $\Phi_i/\Phi_n=5$	> $10^6\text{ }\Omega\text{ cm}^d$
Raman	strong D peak	weak D peak ^b

^aReference 34.

^dReference 35.

^bReference 6.

^bReference 36.

^cReferences 7 and 34.

IV. SUMMARY AND CONCLUSION

Recently, Ulrich *et al.*^{13,37} have prepared c -BN films by rf magnetron sputtering and ion plating with an c -BN content of about 93%. In both cases, the BN and the presently described C films have high fractions of sp^3 bondings. These metastable materials have higher densities than their stable sp^2 modifications, i.e., hexagonal BN and graphite. In both cases it has been shown that low-energy but intense ion bombardment with argon ions the densities of the films can be increased considerably leading to phase transition in both cases to the sp^3 -rich modifications at low temperatures.

Compressive stress in the films arises from ion peening. The compressive stress may be explained in terms of the subplantation model. However, the subplantation model does not explain the energy-dependent sharp maximum in density of the carbon films. Further the lack of densification at low ion energies suggests that (indirect) subplantation process and densification process by argon bombardment have only a small influence on the densification of the C films.

Stress measurements reveal that sp^3 bonded carbon is predominantly deposited for stress values above 14 GPa. The existence of such a stress threshold proves that in the MS/IP a -C films exists a stress-induced transformation from $sp^2 \rightarrow sp^3$ bonded sites. The stress threshold for the deposition of dense carbon films is much higher than the Berman-Simon line which was proposed by McKenzie and co-workers.⁶

The present results indicate strong clustering of sp^3 hybridized carbon. Those sp^3 seeds are responsible for the high density in the carbon films. The electronic properties, such as optical gap and electrical conductivity of the deposited MS/IP carbon films, seem to be predominantly determined by a sp^2 matrix in which sp^3 clusters are embedded.

It follows from our experimental results that, quite generally, by low-energy ion plating at low temperatures any metastable material can be produced, if its density is higher than the density of its stable modification. This is of importance for the production of superhard coatings with C, B, and N,³⁸ consisting of covalent bondings.

ACKNOWLEDGMENT

The authors want to thank Professor Schmoranzner, Physics Department, University of Kaiserslautern, for most valuable support by EELS measurements.

- ¹J. Robertson, *Prog. Solid State Chem.* **19**, 199 (1991).
- ²J. Koskinen, *J. Appl. Phys.* **63**, 2094 (1988).
- ³T. Y. Ishikawa, K. Ogawa, and T. Takagi, *J. Appl. Phys.* **61**, 2509 (1987).
- ⁴Y. Lifshitz, S. R. Kasi, J. W. Rabalais, and W. Eckstein, *Phys. Rev. B* **41**, 10 468 (1990).
- ⁵Y. Lifshitz, G. D. Lempert, E. Grossmann, I. Avigal, C. Uzan-Saguy, R. Kalish, J. Kulik, D. Marton, and J. W. Rabalais, *Diamond Related Mater.* **4**, 312 (1995).
- ⁶D. R. McKenzie, D. Muller, and B. A. Pailthorpe, *Phys. Rev. Lett.* **67**, 773 (1991).
- ⁷P. J. Fallon, V. S. Veerasamy, C. A. Davis, J. Robertson, G. Amaratunga, W. I. Milne, and J. Koskinen, *Phys. Rev. B* **48**, 4777 (1993).
- ⁸J. J. Cuomo, D. L. Pappas, J. Bruley, J. P. Doyle, and K. L. Saenger, *J. Appl. Phys.* **70**, 1706 (1991).
- ⁹N. Savvides, *J. Appl. Phys.* **59**, 4133 (1986).
- ¹⁰J. J. Cuomo, J. P. Doyle, J. Bruley, and J. C. Liu, *Appl. Phys. Lett.* **58**, 466 (1991).
- ¹¹B. Andre, F. Rossi, and H. Dunlop, *Diamond Related Mater.* **1**, 307 (1992).
- ¹²R. Kleber, M. Weiler, A. Krüger, S. Sattel, G. Kunz, K. Jung, and H. Ehrhardt, *Diamond Related Mater.* **2**, 246 (1991).
- ¹³S. Ulrich, J. Scherer, J. Schwan, I. Barzen, K. Jung, and H. Ehrhardt, *Diamond Related Mater.* **4**, 288 (1995).
- ¹⁴W. Dötter, I. Barzen, R. Erz, S. Ulrich, K. Jung, and H. Ehrhardt, *Fresenius J. Anal. Chem.* **1991**, 341.
- ¹⁵H. Ehrhardt, S. Ulrich, I. Barzen, J. Scherer, and K. Jung, *Mater. Wiss. u. Werkstofftech.* **24**, 74 (1993).
- ¹⁶J. Robertson, *Pure Appl. Chem.* **66**, 1789 (1994).
- ¹⁷J. Robertson, *Diamond Related Mater.* **2**, 984 (1993); **3**, 361 (1994).
- ¹⁸C. A. Davis, *Thin Solid Films* **30**, 276 (1993).
- ¹⁹K. J. Takano, H. Harashima, and M. Wakatsuki, *Jpn. J. Appl. Phys.* **30**, L860 (1991).
- ²⁰S. Endo, N. Idani, R. Oshima, K. J. Takano, and M. Wakatsuki, *Phys. Rev. B* **49**, 22 (1994).
- ²¹T. Yagi, W. Utsumi, M. Yamakata, T. Kigegawa, and O. Shimomura, *Phys. Rev. B* **6**, 6031 (1992).
- ²²S. Scandolo, M. Bernasconi, G. L. Chiarotti, P. Focher, and P. Tosatti, *Phys. Rev. Lett.* **74**, 4015 (1995).
- ²³M. Kitabatake, *Diamond Films Technol.* **5**, 41 (1995).
- ²⁴P. C. Kelires, *Phys. Rev. Lett.* **73**, 2460 (1994).
- ²⁵J. Robertson and E. P. O'Reilly, *Phys. Rev. B* **35**, 2946 (1987).
- ²⁶J. Robertson, *Diamond Related Mater.* **4**, 297 (1995).
- ²⁷G. Amaratunga, J. Robertson, V. S. Veerasamy, W. I. Milne, and D. R. McKenzie, *Diamond Related Mater.* **4**, 637 (1995).
- ²⁸S. M. Rossnagel, M. A. Russak, and J. J. Cuomo, *J. Vac. Sci. Technol. A* **5**, 2150 (1987).
- ²⁹P. Koidl, C. Wild, B. Dischler, J. Wagner, and M. Ramsteiner, *J. Mater. Sci.* **52**, 41 (1990).
- ³⁰R. J. Nemanich, T. J. Glass, G. Lucovsky, and R. E. Shroder, *J. Vac. Sci. Technol. A* **6**, 1783 (1988).
- ³¹S. R. P. Silva, G. A. J. Amaratunga, E. K. Salja, and K. M. Knowles, *J. Mater. Sci.* **29**, 4962 (1994).
- ³²J. Wagner, C. Wild, and P. Koidl, *Appl. Phys. Lett.* **59**, 779 (1991).
- ³³S. Sattel, M. Weiler, J. Gerber, T. Giessen, H. Roth, M. Scheib, K. Jung, H. Ehrhardt, and J. Robertson, *Diamond Related Mater.* **4**, 333 (1995).
- ³⁴P. H. Gaskell, A. Saeed, P. Chieux, and D. R. McKenzie, *Phys. Rev. Lett.* **67**, 1286 (1991).
- ³⁵V. S. Veerasamy, G. A. J. Amaratunga, W. I. Milne, J. Robertson, and P. J. Fallon, *J. Non-Cryst. Solids* **164**, 1111 (1993).
- ³⁶M. A. Tamor and W. C. Vassell, *J. Appl. Phys.* **76**, 3823 (1994).
- ³⁷S. Ulrich, J. Scherer, J. Schwan, I. Barzen, M. Scheib, K. Jung, and H. Ehrhardt (unpublished).
- ³⁸H. Ehrhardt, W. Dworschak, S. Ulrich, K. Jung, M. Scheib, and M. Weiler, *New Diamond and Diamondlike Films*, edited by P. Vincenzini (Techna Srl, Faenza, Italy, 1995), p. 191.