First-principles studies of the vibrational properties of amorphous carbon nitrides*

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Raman spectra of amorphous carbon nitride films (a-C:N) resemble those of typical amorphous carbon (a-C), and no specific features in the spectra are shown due to N doping. The present work provides a correlation between the microstructure and vibrational properties of a-C:N films from first principles. The six periodic model structures of 64 atoms with various mass densities and nitrogen contents are generated by the liquid-quench method using Car–Parinello molecular dynamics. By using Raman coupling tensors calculated with the finite electric field method, Raman spectra are obtained. The calculated results show that the vibrations of C=N could directly contribute to the Raman spectrum. The similarity of the Raman line shapes of N-doped and N-free amorphous carbons is due to the overlapping of C=N and C=C vibration bands. In addition, the origin of characteristic Raman peaks is also given.

Keywords: amorphous carbon nitrides, density functional theory, vibrational Raman spectra

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1. Introduction

Since Liu and Cohen[1] first reported that the crystalline β-C_3N_4 might possess hardness exceeding that of diamond, amorphous carbon nitride thin films have been widely investigated. The films have potential applications as thin protective coatings on magnetic hard disks and flat cold cathodes in field emission displays.[2] It is well known that the physical properties of materials strongly depend on their specific microstructure. The a-C:N films have several CN bonding configurations because both carbon and nitrogen can form three hybridization sites (sp, sp^2, and sp^3).[3,4] The structure of a-C:N films can be characterized by many methods, such as diffraction, electron energy loss spectroscopy (EELS), spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), Fourier transform infra-red (FTIR) absorption spectroscopy, and Raman spectroscopy.[5] As a popular, rapid, and non-destructive technique for structural characterization of materials, Raman spectroscopy[6–8] is frequently used to characterize bonding configurations of a-C:N films.

Raman spectra of most amorphous carbons (a-C) show a common broad band[4,9] in the range of 800–2000 cm^{-1}. For visible excitation, this broad band can be empirically decomposed into two peaks,[6] the G peak (around 1560 cm^{-1}) and D peak (around 1360 cm^{-1}). The T peak at around 1060 cm^{-1} can be directly observed in ultraviolet (UV) Raman.[10] Raman spectra of a-C:N resemble those of typical a-C and no specific features in the spectra are shown due to N doping. Therefore, it is now customary to perform most vibrational characterization by adopting the ideas commonly assessed for N-free carbons.[4] However, there is strong evidence for the presence of a third peak at around 1450 cm^{-1} between D and G peaks. This peak has been assigned to a nitrogen-related vibrational peak due to the incorporation of nitrogen atoms in a-C networks.[7,11] It is, therefore, desirable to address the effects of nitrogen doping on the Raman spectra of a-C:N by using theoretical methods.

The Raman spectra of the tetrahedral amorphous carbon (ta-C)[12,13] have been calculated by using a tight-binding method. However, no theoretical Raman studies on a-C:N films have been reported. The main aim of this work is to investigate the relationship between Raman spectroscopy and the bonding structure of a-C:N from first principles. The a-C:N structures are generated with different densities and nitrogen contents by using the liquid-quench technique. The structural optimization is performed through damped first-principle molecular dynamics. Calculations of the vibrational density of states (v-DOS) and Raman spectra are then carried out for these structures. This allows us to correlate the Raman features with the bonding structure.

2. Computational methods

Six model structures of a-C:N were generated by the liquid-quench method using Car–Parinello molecular dynamics (CPMD).[14] The parameters used in this work were the

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same as those of Ref. [15] except that nitrogen atoms replaced some carbon atoms of the initial structure. It was assumed that nitrogen atoms were dispersed in the carbon network, and there were no neighbouring nitrogen atoms in the final structure. There were four steps for modeling the structures of a-C:N: spontaneous melting process, liquid phase equilibrating, cooling process, and solid phase stabilizing. By using a damped molecular dynamics scheme based on the density functional theory, the model structures were subsequently relaxed until the calculated forces on all the atoms were less than 1×10^{-6} Ry/a.u. (1 Ry=13.6056923 eV).

Electronic and structural relaxations were performed using first-principles methods, which were provided in the QUANTUM–ESPRESSO package.[16] Only valence electrons were treated explicitly, while core valence interactions were described by norm-conserving pseudopotentials for C and N. The exchange-correlation energy was accounted for by a local density approximation (LDA).[17] Plane-wave basis sets with energy cutoffs of 55 Ry were used to expand the valence wave functions. Periodic boundary conditions and gamma point sampling of the Brillouin zone were used.

The normalized vibrational modes ξ^n and frequencies ω_n were obtained through the linear-response approach.[18] The Raman scattering processes in the Placzek's approximation were considered. The Raman coupling tensors were calculated by applying finite electric fields of intensity ± 0.001 a.u. to our periodic model structures. The reduced Raman intensities of a-C:N were obtained in the back-scattering geometry. A detailed description of the methodology and the used formulas is given in Refs. [19]– [22].

Because of theoretical simplicity, the calculated intensities should be compared with the measured values using long-wavelength incident light. Taking into account the experimental width of the Raman lines and the finite size of the model, the final spectra were obtained by applying a Gaussian broadening of 50 cm^{-1} to the mode intensities.

3. Results and discussion

Each model generated by liquid quench contains 64 atoms in a periodic cubic cell. The six models are at densities of 2.6, 2.9, and 3.2 g/cm^3 with two nitrogen concentrations (corresponding to two and eight nitrogen atoms in a cell). Upon the damped first-principles relaxation, only minor readjustments of the atomic positions are observed. Figure 1 shows relaxed

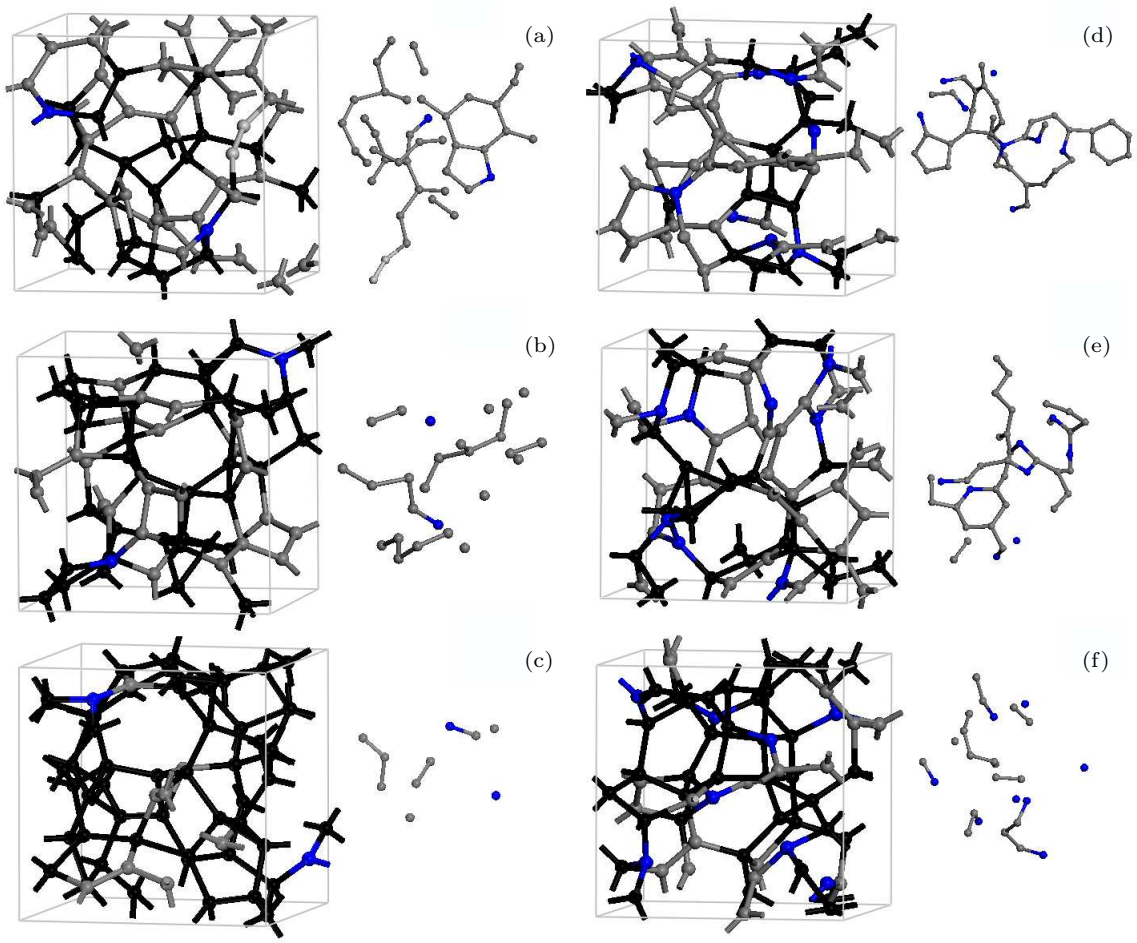


Fig. 1. (color online) Ball-and-stick representation of six a-C:N structures. Black, grey, light grey, and blue atoms denote sp^3 carbon, sp^2 carbon, sp carbon, and nitrogen atoms, respectively.

Table 1. Summary of structural parameters from simulations in this work.

Structure	Carbon/nitrogen ratio	Density /g·cm^{-3}	Bond length/Å		Carbon coordination					Nitrogen coordination		
			C=C	C=N	C_2^0	C_3^0	C_3^+	C_4^0	fourfold/%	N_2^0	N_3^+	N_3^0
A	$C_{62}N_2$	2.61	1.50	1.43	2	38	0	22	35.5	0	0	2
B	$C_{62}N_2$	2.92	1.52	1.43	0	18	6	38	61.3	0	0	2
C	$C_{62}N_2$	3.22	1.54	1.41	0	5	3	54	87.1	0	1	1
D	$C_{56}N_8$	2.65	1.49	1.41	0	37	0	19	33.9	3	0	5
E	$C_{56}N_8$	2.96	1.49	1.40	0	31	0	25	44.6	1	2	5
F	$C_{56}N_8$	3.27	1.51	1.41	0	16	2	38	67.9	2	0	6

The coordination is defined using a cut-off distance of 2.0 Å.

structures of six models using ball-and-stick representation, while Table 1 summarizes some important structural parameters. The nearest-neighbour coordination of an atom is defined as the number of atoms sitting within a sphere of radius 2.0 Å centered on this atom, which is determined from the atomic radius and the radial distribution function.

For fixed N content, the average bond length of C=C and the amount of 4-coordinated carbon (sp^3 C) atoms increase with the mass density. The large rings and long chains of the sp^2 clusters become short chains or dimers (see Fig. 1). The structure with a higher density becomes more compact and disordering. On the other hand, at a fixed mass density, the addition of N leads to the decrease of the average bond length of C=C and the sp^3 C content. Thus, there are more clustering of sp^2 C sites in the structure with a higher N content.

The bonding details for carbon and nitrogen atoms in all simulations are also shown in Table 1. In addition to the neutral C_4^0 (sp^3), C_3^0 (sp^2), and C_2^0 (sp) carbon sites, the threefold coordinated C_3^+ (sp^2) defect sites are also observed in the high intensity structures. In the case of nitrogen, the most common nitrogen site is the uncharged N_3^0 (sp^3) site,[23] where a nitrogen atom forms three single σ bonds and a lone pair of electrons. The second most common nitrogen site is the uncharged N_2^0 (sp^2) site, where a nitrogen atom forms two single σ, one π bond and a lone pair. The charged N_3^+ (sp^2) defect site formed three σ, one π bond, and an unpaired electron, can potentially act as dopant. No onefold- and fourfold-coordinated nitrogen atoms are found.

The v-DOS underlies all the vibrational spectra. We first analyze the v-DOS in terms of the vibrational eigenmodes before addressing Raman spectra. Figures 2(a)–2(f) show the calculated v-DOS and their decompositions of six a-C:N structures from A to F. For the structure A with a density of 2.6 g/cm^3 and a nitrogen content of 3.1 at%, the total v-DOS is decomposed in its partial contributions coming from sp^3 carbon, sp^2 carbon, sp carbon, and N atoms. The sp^2 C vibrations clearly dominate the total v-DOS below 1800 cm^{-1} and show a maximum at $\sim$ 660 cm^{-1}. The sp^3 C vibrations form a peak centered at 1000 cm^{-1}, which dies over 1500 cm^{-1}. Thus, the modes involve only sp^2 carbons in the frequency range from 1500 to 1800 cm^{-1}. The vibrations of the sp carbon chain with a triple bond are responsible for the weak peak around 2100 cm^{-1}. The contribution of N atom vibrations is very small to the total v-DOS of the structure A. For a fixed N content, the decomposition shows that the sp^3 C vibrations increase with the density but the sp^2 C vibrations decrease. On the other hand, the increase of N contents leads to a decrease of the sp^3 C vibrations and an increase of sp^2 C vibrations at a fixed mass density. These results are consistent with changes of the sp^3 and sp^2 carbon contents. For the high-density 3.2 g/cm^3 structures, the vibrational modes below $\sim$1500 cm^{-1} mostly arise from sp^3 C vibrations and the modes at higher frequencies show strong localization of sp^2 carbons. Similar theoretical results have been reported in Refs. [12] and [13], confirming the reliability of our models. There are no distinctive features associated with vibrational localization of nitrogen sites in all the structures that have been found.

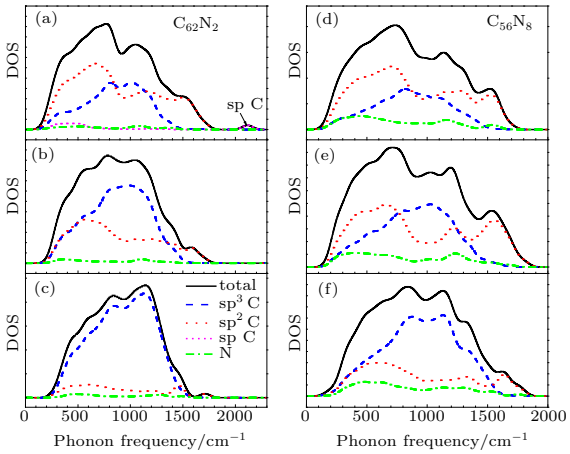


Fig. 2. (color online) Total and partial v-DOS of six a-C:N structures from A to F. We use a Gaussian broadening of 50 cm^{-1} to obtain continuous curves in this figure and in the following figures.

Figures 3(a)–3(f) show the reduced Raman spectra and their decompositions of six a-C:N structures from A to F. This decomposition is achieved by selecting specified components of the vibrational eigenmodes prior to the calculation of the Raman intensities. Unlike the v-DOS, the sum of the partial Raman spectra does not give the full spectrum because of interference terms. However, this decomposition can provide a measure of the relative contributions from various features. It can be seen that Raman spectra are dominated by the sp^2 C sites due to their larger scattering cross sections. Because of

the limited number of sp^2 atoms in our models, the G peaks show a bimodal shape in the A and C structures. The sp carbon chain results in a weak C peak at 2100 cm^{-1}, and the peak position is consistent with the experimental data.[24] A small T peak centered at 1000 cm^{-1}, which results from the sp^3 C=C vibrations, can be observed. Moreover, there is a prominent D peak in the structure D with the highest sp^2 content. For a fixed nitrogen content, the G peak position moves to a high wave number with the increasing density. While when the mass density is fixed, the G-peak position with different nitrogen contents is almost unchanged.[4,25]

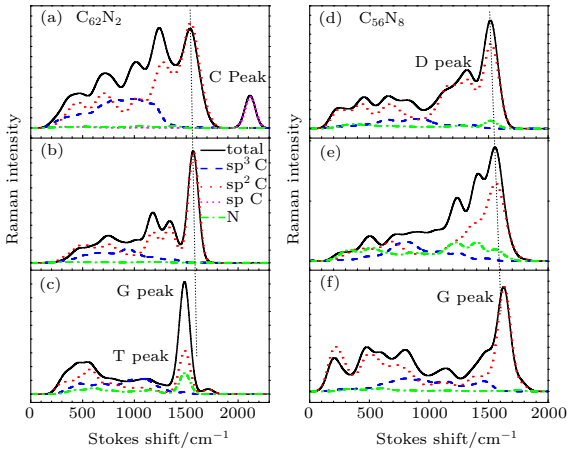


Fig. 3. (color online) Total and partial Raman spectra (a)–(f) for six a-C:N structures from A to F.

Because of the obvious contribution of nitrogen vibrations to the Raman spectra in the structures $C_{62}N_2$-3.22, $C_{56}N_8$-2.65, and $C_{56}N_8$-2.96, we now consider the role of nitrogen in the Raman spectra. Figure 4 shows the decomposition of nitrogen weight into N_2^0, N_3^0, and N_3^+ sites for the structure $C_{62}N_2$-3.22, $C_{56}N_8$-2.65, and $C_{56}N_8$-2.96, respectively. The vibrational modes above 1500 cm^{-1} appear to originate almost exclusively from N_2^0 and N_3^+ sites, whereas N_3^0 sites only contribute to the rest of the spectrum. This indicates that the vibrational contribution of N atoms to the high frequency modes might result from the carbon–nitrogen double bond in N_2^0 and N_3^+ sites. Therefore, the Raman vibrations arising from all pairs of sp^2 atoms in both olefinic chains and rings, atoms with the C=C double bonds, and atoms with the C=N double bonds are investigated and shown in Fig. 5. It is obviously that the G peak is due to the bond stretching motion of all pairs of sp^2 sites. Moreover, the Raman vibrations of CN are significant. Because the vibrational frequencies of the C=N stretching mode are very close to those of the C=C stretching mode, the main Raman features resemble those observed in N-free carbon films. The obtained results also give the reason of the G-peak shift. When the sp^2 sites change their configuration from large rings to short chains, the vibration frequency moves towards the frequency of the C=C or C=N dimers embedded in the C=C sp^3 matrix. The C=C or C=N bond length in the chains or dimers is shorter, so the G peak lies at a higher frequency.

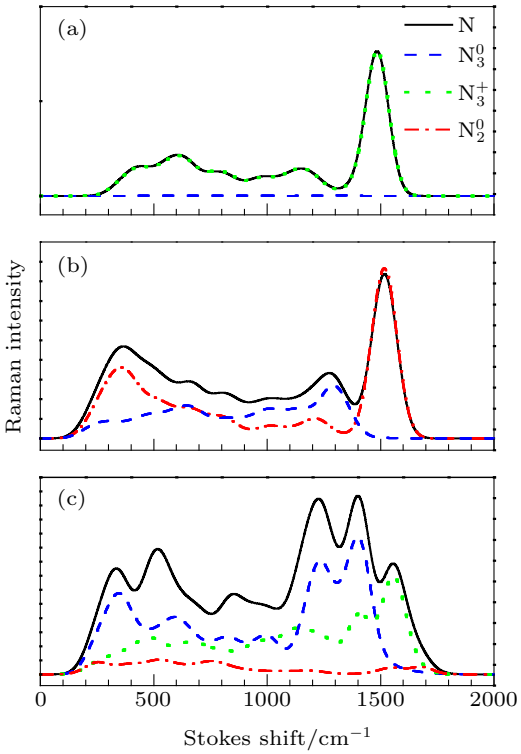


Fig. 4. (color online) Partial Raman spectra of nitrogen and decomposition for the structures (a) $C_{62}N_2$-3.22, (b) $C_{56}N_8$-2.65, and (c) $C_{56}N_8$-2.96, respectively.

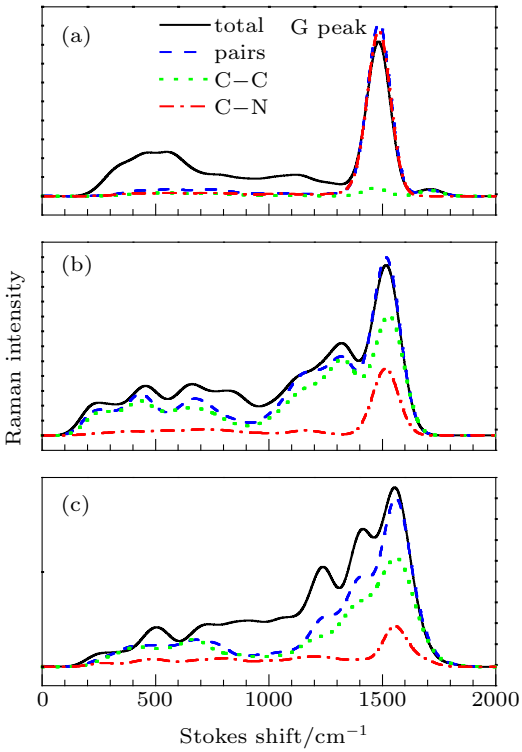


Fig. 5. (color online) Raman spectra and decomposition for the structures (a) $C_{62}N_2$-3.22, (b) $C_{56}N_8$-2.65, and (c) $C_{56}N_8$-2.96, respectively.

In general, the presence of the D peak indicates the presence of sixfold aromatic rings.[26] However, the results of Ref. [27] show that the D peak can arise from odd rings and especially fivefold ones. These odd rings break the D_{6h} symmetry of aromatic rings and exhibit a dipolar moment, resulting

in a nonvanishing contribution to the first order Raman spectrum. In order to confirm these results, the sp^2 C vibrations of the Raman spectrum are decomposed according to the fivefold and sixfold rings in the $C_{56}N_8$-2.65 structure (see Fig. 6). The calculated results show that the fivefold ring has a strong contribution to the D peak. It confirms that the D peak is due to the breathing modes of sp^2 atoms in rings.

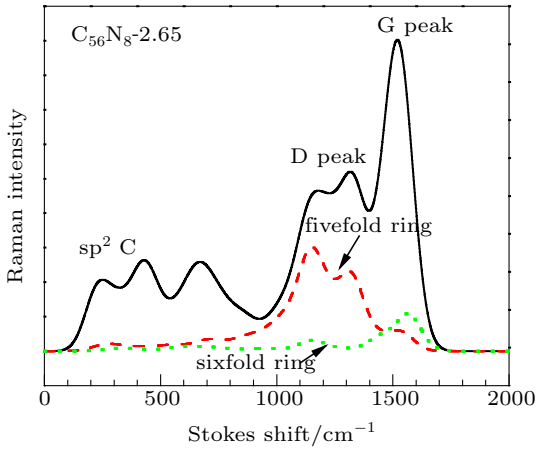


Fig. 6. (color online) Further decomposition of the sp^2 carbon Raman spectra for the structure $C_{56}N_8$-2.65.

4. Conclusions

Using a first-principles approach, we calculated reduced Raman spectra of six a-C:N structures with different nitrogen contents at three densities of 2.6, 2.9, and 3.2 g/cm^3. The microstructure, vibrational properties, and their relations were investigated. The analysis in terms of atomic vibrations indicates that the direct contribution of CN vibrations to the Raman spectrum is significant, and it results mainly from the carbon–nitrogen double bonds in sp^2-type nitrogen atoms. Because of the overlapping of the C=N and C=C vibration bands, it is difficult to distinguish vibrational modes due to C or N atoms in the experimental analysis. The results confirm that the G peak arises from stretching vibrations of all pairs of sp^2-type atoms and the C peak arises from the C≡C sp vibrations. The T peak is due to the C=C sp^3 vibrations, and the D peak is due to the breathing modes of sp^2 atoms in rings, including fivefold and sixfold rings.

References

[1] Liu A and Cohen M L 1989 *Science* **245** 841
[2] Silva S R P, Amaratunga G A J and Barnes J R 1997 *Appl. Phys. Lett.* **71** 1477
[3] Silva S R P, Robertson J, Amaratunga G A J, Rafferty B, Brown L M, Schwan J, Franceschini D F and Mariotto G 1997 *J. Appl. Phys.* **81** 2626
[4] Ferrari A C, Rodil S E and Robertson J 2003 *Phys. Rev.* B **67** 155306
[5] Robertson J 2002 *Mater. Sci. Eng.* R-*Rep.* **37** 129
[6] Tamor M A and Vassell W C 1994 *J. Appl. Phys.* **76** 3823
[7] Das D, Chen K H, Chattopadhyay S and Chen L C 2002 *J. Appl. Phys.* **91** 4944
[8] Xing H Y, Niu P J and Xie Y X 2012 *Chin. Phys.* B **21** 077801
[9] Wang Y J, Li H X, Ji L, Liu X H, Wu Y X, Zhou H D and Chen J M 2012 *Chin. Phys.* B **21** 016101
[10] Ferrari A C and Robertson J 2001 *Phys. Rev.* B **64** 075414
[11] Chowdhury A K M S, Cameron D C and Hashmi M S J 1998 *Thin Solid Films* **332** 62
[12] Profeta M and Mauri F 2001 *Phys. Rev.* B **63** 245415
[13] Piscanec S, Mauri F, Ferrari A C, Lazzeri M and Robertson J 2005 *Diamond Relat. Mater.* **14** 1078
[14] Computer code CPMD (Car-Parrinello molecular dynamics), copyright IBM Corp., 1990–2001, copyright MPI für Festkörperforschung, Stuttgart, 1997–2005 (http://www.cpmd.org)
[15] Han J C, Gao W, Zhu J Q, Meng S H and Zheng W T 2007 *Phys. Rev.* B **75** 155418
[16] Giannozzi P, Baroni S and Bonini N 2009 *J. Phys.*: *Condens. Matter* **21** 395502
[17] The "C.pz-vbc.UPF" and "N.pz-vbc.UPF" from the PWscf table (http://www.pwscf.org/pseudo.htm) were used for carbon and nitrogen, respectively.
[18] Giannozzi P, de Gironcoli S, Pavone P and Baroni S 1991 *Phys. Rev.* B **43** 7231
[19] Umari P and Pasquarello A 2002 *Phys. Rev. Lett.* **89** 157602
[20] Giacomazzi L, Umari P and Pasquarello A 2006 *Phys. Rev.* B **74** 155208
[21] Niu L, Zhu J Q, Gao W, Liu A P, Han X and Du S Y 2008 *Physica* B **403** 3559
[22] Zhou B, Su Q and He D Y 2009 *Chin. Phys.* B **18** 4988
[23] Merchant A R, McKenzie D R and McCulloch D G 2001 *Phys. Rev.* B **65** 024208
[24] Ravagnan L, Siviero F, Lenardi C, Piseri P, Barborini E and Milani P 2002 *Phys. Rev. Lett.* **89** 285506
[25] Shi J R, Shi X, Sun Z, Liu E, Tay B K and Lau S P 2000 *Thin Solid Films* **366** 169
[26] Ferrari A C and Robertson J 2000 *Phys. Rev.* B **61** 14095
[27] Lejeune M, Bouzerar R, Benlahsen M, Durand-Drouhin O and Zeinert A 2001 *Appl. Phys. Lett.* **79** 3443