

Calculated electronic density of states and structural properties of tetrahedral amorphous carbon

K. Jarmo Koivusaari ^{a,*}, Tapio T. Rantala ^b, Seppo Leppävuori ^a

^a *Microelectronics and Material Physics Laboratory and EMPART Research Group of Infotech Oulu, Department of Electrical Engineering, University of Oulu, PL 4500, FIN-90401 Oulu, Finland*

^b *Department of Physical Sciences, University of Oulu, PL 3000, FIN-90401 Oulu, Finland*

Abstract

A series of tetrahedral amorphous carbon structures with different microscopic mass densities was generated by calculations based on the density functional theory with a local density approximation and using a method of melting–cooling cycles. A detailed investigation of the properties of the simulated structures has been carried out. Particularly, the short-range order, nearest neighbour distances, fractions of sp^1 , sp^2 and sp^3 sites, average C–C–C bond angles and electronic density of states have been analysed. The simulated structures and calculated properties are in good agreement with those obtained by others and with the experimental data. An unexpected observation is the presence of planar structures, which are typical for graphite, in the sample with low density. In addition, the nearest neighbour distance in the sample with mass density 3.54 g/cm^3 is different from those reported previously. Possibilities to compare the density of states obtained from the simulations with the experimental results from scanning tunnelling spectroscopy and X-ray near edge spectrum are discussed. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Computer simulation; Density of states; Diamond-like carbon; Modelling

1. Introduction

The importance of tetrahedral amorphous carbon (ta-C) has been suggested by reports of its unique mechanical [1] and electronic properties [2–4]. Depending on the way it is formed, the ta-C can be electrically conducting, or semiconducting. Other properties of the ta-C include heat and radiation resistance, optical transparency over a wide spectral range, chemical inertness and low or negative electronic affinity. The most dramatic progress and success of the mechanical applications have involved the ta-C coated cutting tools and moving parts of machines. Environments where they are used are often hostile, components are required to withstand drastic wear, and abrasion resulting from sliding and turning. Clearly, hard and smooth protective ta-C coatings would increase the lifetime of the parts against erosion. Further, the decreased need for frequent servicing would substantially reduce costs associated with the machine maintenance.

The extraordinary electronic properties of ta-C and the predicted advantages for high frequency and high power electronic applications have initiated significant interest in making ta-C based electronic applications. Another attractive field is high temperature electronics. The ta-C could have significant advantages over conventional materials such as GaAs, primarily because it has low junction current leakage and exhibits complete channel current pinch-off and modulation [5,6]. Based on the above, the ta-C could provide a new material for many electronic applications, such as microsensors for hostile environments, heat sinks for high power electronics, thin flat-panel displays or cold cathodes based on a field-emission, and faster, more powerful transistors and circuits that could operate at gigahertz speeds. Many of these applications need extensive study to meet the requirements of the applications with significant market potential.

The random tetrahedral networks formed by the amorphous silicon and amorphous germanium that are completely tetrahedrally bonded, i.e. sp^3 hybridised, can be modelled with the so-called *tetrahedral glass model* (TGM) [7]. Compared with the ideal random tetrahe-

* Corresponding author. Fax: +358-8-5532728.

E-mail address: jarmo.koivusaari@oulu.fi (K.Jarmo Koivusaari)

dral networks, the ta-C structures have at least 10% sp^2 sites, i.e. three-fold coordinated atoms. Therefore, the TGM cannot be applied to model ta-C, and so far, despite the progress of computer simulated models during recent years, there is no generally accepted structural model for ta-C.

2. Current state of simulations

Structural properties of the ta-C have been calculated using empirical interatomic potentials [8–10]. These calculations suggest that the sp^3 -bonded form of ta-C has considerably higher energy than the sp^2 -bonded form. In addition, microscopic mass density and bond distances have been successfully modelled [11]. Using this relatively simple approach, Kaukonen and Nieminen [12] predicted that deposited ions with energies of 40–70 eV result in the highest sp^3 fraction. However, it has been shown experimentally and theoretically that higher ion energies, up to 500 eV, are needed to produce ta-C films with a high (~ 75 –90%) sp^3 fraction [13–16].

Fraunheim et al. [17–19] used both purely empirical potentials and semi-empirical tight-binding (TB) schemes in their hybrid density functional non-orthogonal TB method. They concluded that the sp^3 fraction of the ta-C increases as the density increases, reaching a maximum, 88%, at density 3.5 g/cm³. In addition, the fraction of π states in the density of states (DOS) lowers considerably as the mass density increases.

One of the first attempts to calculate the electronic structure, DOS and structure of ta-C was made by Robertson and O'Reilly [2]. It was shown that the presence of sp^3 sites was insufficient to produce an optical band gap.

Wang et al. [20–23] used an orthogonal tight-binding molecular dynamics (TBMD) scheme in which electronic structure effects were incorporated through the TB parameterisation to study structural and electronic properties of the ta-C. This reduced the number of required atomic orbitals per atom and allowed a larger number of the atoms to be treated in calculations. Structures with the high sp^3 fraction were generated using high mass densities, such as 4.4 g/cm³, which were later rescaled to lower values.

A local orbital *ab initio* method and 64 atom unit cell were applied by Drabold et al. [24,25] to study ta-C. They generated a ta-C structure with a density of 3.0 g/cm³ and found an sp^3 fraction of 85% and a defect-free 2 eV band gap.

In recent papers, Marks et al. reported the first full *ab initio* MD calculations completed for ta-C [26,27]. Simulations show the presence of the three- and seven-membered rings. The presence of three-membered rings was reported for the first time. In addition, the number

of seven-membered rings was smaller than previously. These ring structures gave the network an unusual topology. The observation that the sp^3 fraction increases at faster quench rate was clearly demonstrated [26,27].

In a recent work by Schultz and Stechel [28] it was shown that a minimum basis set is inadequate to negotiate breaking and making bonds while relaxing the structure. Therefore, a high quality basis set must be used in calculations.

3. Computational methods and analysis

In this paper, we present a systematic study of the correlation between electronic DOS, short-range order, sp^2/sp^3 bond ratio and average bond angles of simulated ta-C structures. A series of ta-C structures with different microscopic mass density was generated by running molecular dynamics for a melting-cooling cycle and using the density functional theory (DFT) with a local density approximation (LDA) [29,30]. The Harris functional formalism was used to evaluate the energetics for molecular dynamics. It offers a fast algorithm for evaluation of forces from DFT [31]. The time limiting step in the Harris functional approximation is the solution of a one-particle Schrödinger equation. However, compared with the full Kohn–Sham formalism [29], only one solution is needed for a given set of nuclear locations. This speeds up the calculation roughly equal to the number of iterations required for energy expression in the Kohn–Sham formalism to become self-consistent. All simulations were carried out using commercially available software [32].

The initial configuration of atoms was a simple periodic cubic lattice with diamond structure. A unit cell with 64 atoms was chosen to allow comparison with work carried out by others. The density of the sample was controlled by choosing the lattice constants. We chose sample densities from the typical graphite density, 2.0 g/cm³, to the experimental diamond density, 3.54 g/cm³. The initial lattice structure was melted by raising the temperature, within 100 fs, from 300 K to 6300 K. At 6300 K the samples became completely liquid, as confirmed by calculating the radial distribution function (RDF) of the samples. At this state the liquid was equilibrated for 10 fs in order to ensure a completely molten state. After equilibration, the sample was quenched back to 300 K within 100 fs. After quenching, the structures were further equilibrated for 50 fs. Several runs were completed with similar simulation conditions in order to ensure the reproducibility of the results. We chose to use a quench rate of 10^{15} K/s in order to make our results comparable with those obtained by others.

The radial distribution function $g(r)$ provides useful information about the simulated amorphous networks which can be compared with the experimental data. It

is defined by

$$g(r) = \left\langle \frac{\rho(r)}{\rho_0} \right\rangle \quad (1)$$

where $\rho(r)$ is the density of neighbouring atom centres at a distance of r from an atom, ρ_0 is the overall density and the average, $\langle \rangle$, is evaluated over all atom centres in the system. The coordination number was determined counting all neighbouring atoms within the distance 1.75 Å. This definition is used throughout the rest of the paper, in particular where hybridisation is considered.

4. Results

In Fig. 1. we show the final annealed structure with mass density of 2.0 g/cm³. We see that the structure contains mainly planes of chains which are weakly cross-linked. This planar structure is typical for graphite and is not observed in the samples with mass density higher than 2.3 g/cm³.

The nearest neighbour distance, shown in Fig. 2, is determined by the first peak in the RDF. It increases from 1.41 Å, reaching a plateau value of 1.5 Å, with the mass density higher than 2.7 g/cm³. These values are close to the tabulated C–C graphite and diamond bond lengths, 1.426 Å and 1.541 Å, respectively. At the mass density of 3.54 g/cm³, we observed slightly shorter nearest neighbour distances. The two insets show typical RDF curves at mass densities 2.0 g/cm³ and 3.54 g/cm³.

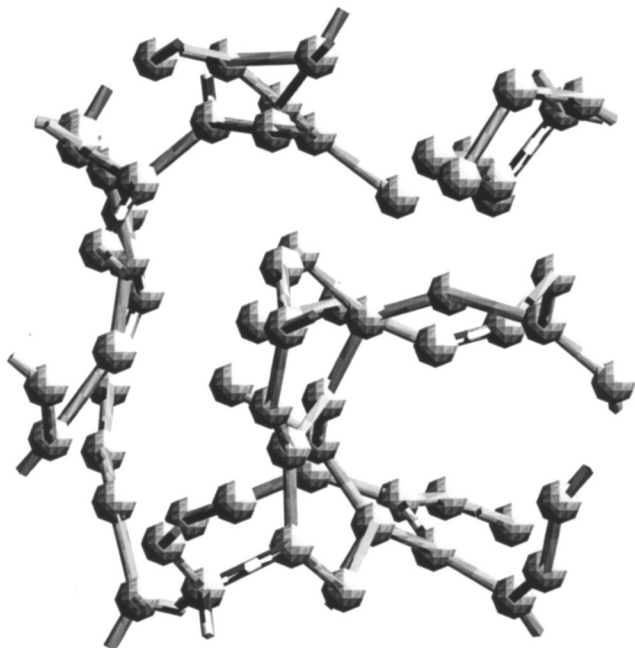


Fig. 1. Low-density structure of ta-C (2.0 g/cm³). Note the planar structures that are typical for graphite.

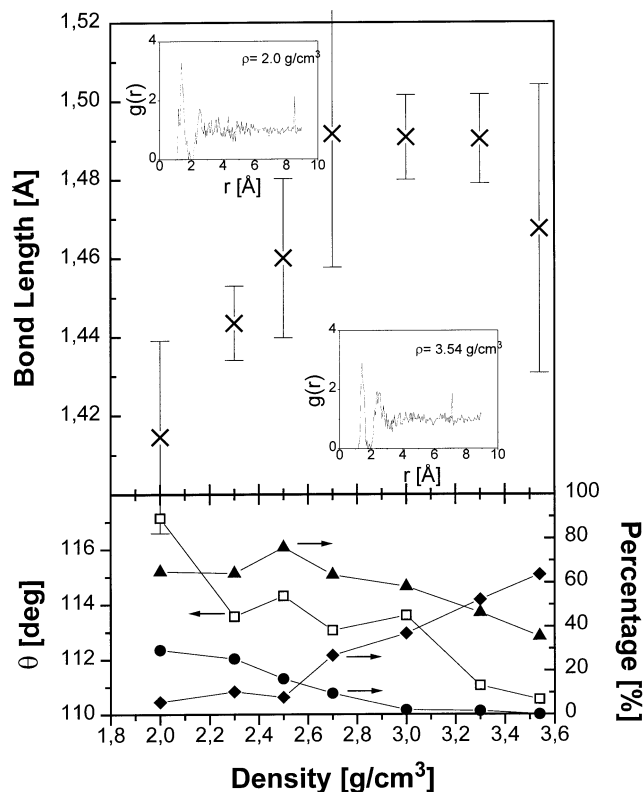


Fig. 2. Top: average nearest neighbour distance as a function of mass density. Two insets show typical radial distribution functions of the samples with mass density of 2.0 g/cm³ and 3.54 g/cm³. The error bars show the standard error of mean of several samples. Bottom: average bond angles ($\square$), sp^1 ($\bullet$), sp^2 ($\blacktriangle$), and sp^3 ($\blacklozenge$) fractions as a function of mass density.

The mass densities of the amorphous networks with corresponding C–C–C bond angles and sp^1 , sp^2 and sp^3 contents are also represented in Fig. 2. We note that the average bond angle decreases from 117° to 110° as the mass density increases. The average bond angle of the sample with mass density of 2.0 g/cm³ is slightly smaller than in the graphitic honeycomb lattice, while the average bond angle of the sample with the highest density is very close to the tetrahedral bond angle, i.e. 109.47°. The bond angle distributions, not shown here, were broad, ranging from 80° to 140°. The two-fold coordinated, sp^1 , atom content decreases along with the three-fold coordinated, sp^2 , atom content with increasing mass density. Although the sp^1 content decreases and the sp^3 content increases almost linearly, we see non-linear behaviour in the change of sp^2 content. At mass density 2.5 g/cm³ the increase in sp^2 content may indicate cross-linking of the chain structure which was not present in the samples with lower mass density.

We also evaluated the DOS of the samples. In Fig. 3, we show the calculated DOS for the selected mass densities. In addition, the experimental X-ray absorption near edge structures (XANES) for highly oriented pyrolytic graphite (HOPG) and diamond-like carbon (DLC)

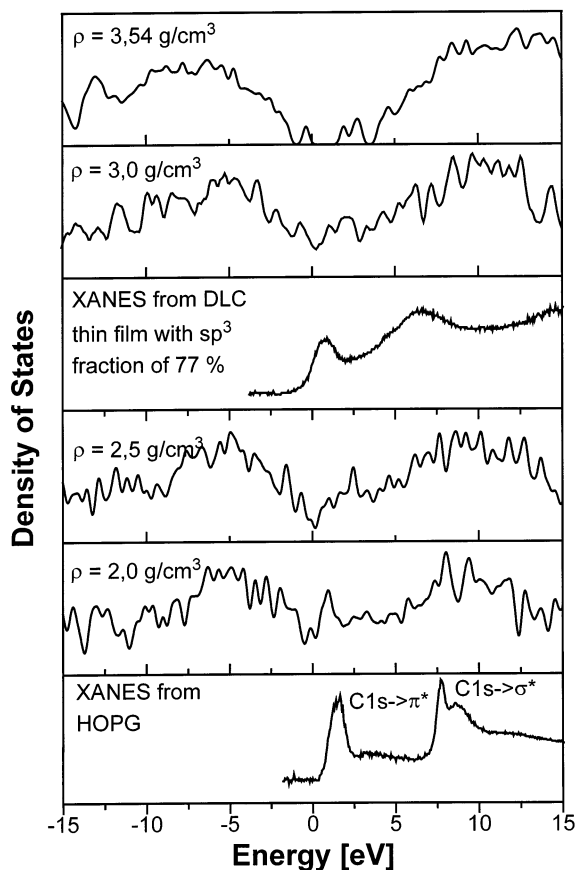


Fig. 3. Calculated DOS for the selected mass densities and experimental XANES [13] from HOPG and DLC thin film with sp^3 fraction of 77%. The Fermi level is located at 0 eV. The XANES have been shifted in energy by 284.4 eV, which is the binding energy of the C1s photoemission, in order to model conduction band DOS.

thin film with sp^3 fraction of 77% are shown. The Fermi level is set to 0 eV. In the sample with mass density 2.0 g/cm^3 we find clear π^* state at the bottom of the conduction band, and as the mass density increases the π^* state fades away. In the sample with mass density 3.54 g/cm^3 , we find a clear band gap with two gap states, which are typical for highly amorphous structures. We find interesting similarities between the calculated DOS and the experimental XANES spectra. The excitations from the ground C1s to the π^* and σ^* states in the XANES spectrum from HOPG compare well with the π^* and σ^* states in calculated DOS of the sample with mass density 2.0 g/cm^3 . The XANES spectrum from the DLC thin film with sp^3 fraction of 77% also has remarkable similarities to the calculated DOS of the sample with mass density 3.0 g/cm^3 .

5. Discussion

The simulated structures are in good agreement with experiments, particularly with regard to the bond angle

and the sp^2/sp^3 fraction, which clearly show how the properties of the simulated structure undergo transformation from the typical graphite values towards the typical diamond values. The nearest neighbour distance also shows a similar trend. The smaller value of the nearest neighbour distance at mass density 3.54 g/cm^3 is not surprising, since compared with perfect diamond crystal, a simulated amorphous network was generated using a fast cooling rate. Therefore, the atoms had no time to find locations that are energetically most favourable. The observed sp^3 fraction is also somewhat smaller than the experimental ones. This may originate from the fact that in the real thin film deposition there is a high-energy particle bombardment initial to the film surface, which causes internal stress in the growing film. The internal stress in the growing film enhances the sp^3 bonding of the atoms [13,33].

Let us now turn to the investigation of the electronic properties of the calculated structures. The structural properties of the theoretically calculated ta-C networks show that with increasing mass density the generated structures maintain properties that are more diamond-like. In Fig. 3, we show the DOS of the calculated structures together with the XANES spectra from HOPG and DLC thin film with sp^3 fraction of 77%. The Gaussian broadening with a line width of 0.5 eV is used for smoothing. The XANES spectra have been shifted in energy by 284.4 eV, which is the binding energy of the C1s photoemission, to model the conduction band DOS.

The electronic properties of the ta-C structures are controlled by π and π^* states, which lie close to the Fermi level, whereas the mechanical properties are controlled by σ and σ^* states. Therefore, we are mainly interested in the π and π^* states. With the increasing mass density, the fraction of the π states lowers significantly. At mass density 3.54 g/cm^3 , the π states have faded away, leaving only two band gap states, which are typical of amorphous networks. These findings are in good agreement with experimental results [13], which showed that the relative intensity of the excitation from the ground C1s to the π^* state decreases with increasing sp^3 fraction. The C1s $\rightarrow \pi^*$ and C1s $\rightarrow \sigma^*$ excitation observed in the XANES from HOPG (Fig. 3) compares well with the π^* and σ^* states in the calculated DOS of the sample with mass density 2.0 g/cm^3 . The C1s $\rightarrow \pi^*$ excitation in the XANES, however, does not correspond directly to the density of π^* states, since its lower edge is excitonically enhanced [2–4]. Also, the XANES from DLC with sp^3 fraction of 77% compares well with the calculated DOS of the sample with mass density 3.0 g/cm^3 . The small shift of transitions in the XANES towards the Fermi level is most likely due to the excitonic effect described above.

In the low density limit sample (see Fig. 2) we see planar ring structures that are typical of graphite. As the density increases above 2.3 g/cm^3 , these planar ring

structures are no longer observed. Equally, in the DOS of the low density limit sample we see clear π^* states, which fade away as the density decreases. Hence, we believe that in ta-C, disordered graphite-like planar ring structures give rise to π states as expected.

We are currently starting surface DOS calculations along with scanning tunnelling spectroscopy (STS) measurements for ta-C samples. Similar work was recently accomplished by Arena et. al. [34]. Our preliminary current–voltage characteristic measurements on the samples produced by pulsed laser deposition on n-Si substrates with low and high sp^3 fraction show significant differences. With the low sp^3 fraction, the I – V curve has symmetrical shape with both positive and negative bias scan region, while with the high sp^3 fraction rectifying characteristics were observed. A similar effect was observed earlier from amorphous diamond (a-D) [35], and indicates that the undoped a-D thin films with high sp^3 fraction are intrinsically p-type semiconductor materials. The ta-C on n-Si forms an ideal p–n heterojunction, with negative bias applied on the n-Si operating as a forward-biased cathode emitter [35].

6. Conclusions

The present simulations of ta-C structures with varying densities clearly show the trend of increasing diamond-like properties with increasing density. At low density limit the simulations lead to a disordered layer structure similar to that of graphite. With increasing density the average bond length, bond angle and sp^1 , sp^2 and sp^3 fractions all come closer to those of diamond-like amorphous carbon.

The variations in electronic structure seen in the DOS show the same tendency. At the low density limit $Cl s \rightarrow \pi^*$ and $Cl s \rightarrow \sigma^*$ transitions in XANES from HOPG compare well with π^* and σ^* states in our calculated DOS. There is no band gap, either, at the low density limit. The XANES from DLC with sp^3 fraction of 77% has similar shape to the calculated DOS of the sample with mass density 3.0 g/cm^3 . Furthermore, at the high density limit there is a wide band gap with two band gap states.

In general, our results are in agreement with experiments. In addition, the present study provides a detailed understanding of the origins of the ta-C relationships between the structural and electronic properties of the ta-C with varying density.

Acknowledgement

Discussions with Juhani Levoska are gratefully acknowledged. One of the authors, KJK, appreciates the financial support of the Jenny and Antti Wihuri Foundation, Tauno Tönning Foundation, Tekniikan

Edistämisen säätiö and Finnish Cultural Foundation. All simulations were run on computers at the Center for Scientific Computing (CSC, Espoo, Finland) under Research Project oyl106.

References

- [1] F. Davanloo, C.B. Collins, K.J. Koivusaari, *J. Mater. Res.* (1999) in press, and references cited therein.
- [2] J. Robertson, E.P. O'Reilly, *Phys. Rev. B* 35 (1987) 2946.
- [3] J. Robertson, in: J.C. Angus, R.E. Clausing, L.L. Horton, P. Klöidl (Eds.), *Diamond and Diamond-Like Films and Coatings*, Plenum Press, New York, 1991.
- [4] J. Robertson, *Surf. Coat. Technol.* 50 (1992) 185.
- [5] L.Y.S. Pang, S.S.M. Chan, C. Johnston, P.R. Chalker, R.B. Jackman, *Diamond Relat. Mater.* 6 (1997) 333.
- [6] A.J. Clough, W.I. Milne, B. Kleinsorge, J. Robertson, G.A.J. Amaratunga, B.N. Roy, *Electron. Lett.* 32 (1996) 498.
- [7] J.M. Ziman, in: *Models of Disorder*, Cambridge University Press, Cambridge, 1979, pp. 447–454.
- [8] J. Tersoff, *Phys. Rev. Lett.* 56 (1986) 632.
- [9] J. Tersoff, *Phys. Rev. B* 37 (1988) 6991.
- [10] J. Tersoff, *Phys. Rev. Lett.* 64 (1990) 1757.
- [11] P.C. Kelires, *Phys. Rev. Lett.* 68 (1992) 1854.
- [12] H.-P. Kaukonen, R.M. Nieminen, *Phys. Rev. Lett.* 68 (1992) 620.
- [13] K.J. Koivusaari, J. Levoska, S. Leppävuori, *J. Appl. Phys.* 85 (1999) 2915.
- [14] Y. Lifshitz, S.R. Kasi, J.W. Rabalais, *Phys. Rev. Lett.* 62 (1989) 1290.
- [15] Y. Lifshitz, S.R. Kasi, J.W. Rabalais, *Phys. Rev. B* 41 (1990) 10468.
- [16] Y. Lifshitz, S.R. Kasi, J.W. Rabalais, *Phys. Rev. Lett.* 62 (1989) 1290.
- [17] Th. Frauenheim, G. Jungnickel, U. Stephan, P. Blaudeck, S. Deuschmann, M. Weiler, S. Sattel, K. Jung, H. Ehrhardt, *Phys. Rev. B* 50 (1994) 7940.
- [18] J. Schäfer, J. Ristein, R. Graupner, L. Ley, U. Stephan, Th. Frauenheim, V.S. Veerasamy, G.A. Amaratunga, M. Weiler, H. Ehrhardt, *Phys. Rev. B* 53 (1996) 7762.
- [19] Th. Frauenheim, U. Stephan, P. Blaudeck, G. Jungnickel, *Diamond Relat. Mater.* 3 (1994) 462.
- [20] C.Z. Wang, K.M. Ho, C.T. Chan, *Phys. Rev. Lett.* 70 (1993) 611.
- [21] C.Z. Wang, K.M. Ho, *Phys. Rev. Lett.* 71 (1993) 1184.
- [22] C.H. Xu, C.Z. Wang, C.T. Chan, K.M. Ho, *Phys. Rev. B* 47 (1993) 9878.
- [23] C.Z. Wang, K.M. Ho, C.T. Chan, *Phys. Rev. B* 47 (1993) 14835.
- [24] D.A. Drabold, P.A. Fedders, P. Stumm, *Phys. Rev. B* 49 (1994) 16415.
- [25] D.A. Drabold, P.A. Fedders, M.P. Grumbach, *Phys. Rev. B* 54 (1996) 5480.
- [26] N.A. Marks, D.R. McKenzie, B.A. Pailthorpe, M. Bernasconi, M. Parrinello, *Phys. Rev. Lett.* 76 (1996) 768.
- [27] N.A. Marks, D.R. McKenzie, B.A. Pailthorpe, M. Bernasconi, M. Parrinello, *Phys. Rev. B* 54 (1996) 9703.
- [28] P.A. Schultz, E.B. Stechel, *Phys. Rev. B* 57 (1998) 3295.
- [29] W. Kohn, L.J. Sham, *Phys. Rev. A* 140 (1965) 1133.
- [30] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [31] J. Harris, *Phys. Rev. B* 31 (1985) 1770.
- [32] FastStructure code under CERIU2 interface, Molecular Simulations Inc., Cambridge, UK.
- [33] J.J. Cuomo, D.L. Pappas, J. Bruley, J.P. Doyle, K.L. Saenger, *J. Appl. Phys.* 70 (1991) 1706.
- [34] C. Arena, B. Kleinsorge, J. Robertson, W.I. Milne, M.E. Welland, *J. Appl. Phys.* 85 (1999) 1609.
- [35] W.N. Wang, N.A. Fox, D. Richardson, G.M. Lynch, J.W. Steeds, *J. Appl. Phys.* 81 (1997) 1505.