PHYSICAL REVIEW B **79**, 224203 (2009)

Modeling noncrystalline materials: Use of vibrational spectra as a protocol for validation

F. Gaspari,[1,*] I. M. Kupchak,[1,2] A. I. Shkrebtii,[1] and J. M. Perz[1]
[1]*University of Ontario Institute of Technology, Oshawa, Ontario, Canada L1H 7L7*
[2]*V. Lashkarev Institute of Semiconductor Physics NAS, Kiev 03028, Ukraine*

(Received 21 April 2009; published 16 June 2009)

Noncrystalline materials are important systems that can be investigated by molecular dynamics (MD); the constant improvement of computing capacity and speed makes it possible to employ MD simulations for the derivation of fundamental macroscopic properties from microdynamics. Hydrogenated amorphous silicon represents a good test material for simulation due to the extensive literature on its optoelectronic properties, and many variants of MD have been attempted to describe this material and to obtain information on its macroscopic properties. As MD is increasingly used to characterize noncrystalline materials, it is crucial to verify that the numerical model is consistent with experimental data. However, in most cases the only derived property used to test the "realism" of the models has been the radial distribution function (RDF). We report extensive *ab initio* simulation of hydrogenated amorphous silicon that demonstrates that, although agreement with the RDF is a necessary requirement, this protocol is insufficient for the validation of a model; we show that the derivation of realistic vibrational spectra is a more efficient and valid protocol to ensure the reproducibility of macroscopic experimental features.

DOI: 10.1103/PhysRevB.79.224203 PACS number(s): 71.15.Pd, 63.50.Lm, 78.20.Bh

I. INTRODUCTION

Important macroscopic properties of noncrystalline systems include the radial distribution function (RDF), bond-angle distribution, vibrational spectra, and optical gap. Hydrogenated amorphous silicon (a-Si:H), a prominent disordered material that has been the subject of intensive investigation for at least 30 years, and for which there exists an extensive literature covering all of its most important properties,[1,2] provides a good test for the verification of the validity of a particular model. Due to its importance in photovoltaics[2,3] and microelectronics, many theoretical techniques have been employed to establish a realistic microscopic model of a-Si:H, including classical[4,5] density-functional-based tight-binding molecular dynamics (MD),[6,7] and *ab initio* molecular dynamics (AIMD).[8,9] Some of these simulation have been used recently to investigate important processes in a-Si:H, including hydrogen dynamics and the Staebler-Wronski effect.[10] However, verification of the "realism" of the models has mostly been limited to the well-established procedure of derivation of the RDF and its comparison with experimental data.

For instance, Su and Pantelides[9] use AIMD to simulate a-Si:H and to analyze H diffusion, employing the RDF to validate the model. As a result, they incorrectly relate the frequency of H migration between two Si atoms to the experimentally observed 2000–2100 cm^{-1} frequency range, the most significant hydrogen signature in amorphous silicon (a more detailed discussion on this feature will follow).

Tuttle[11] calculates the properties of hydrogen in crystalline silicon and in a realistic model of hydrogenated amorphous silicon by using the tight-binding method, parametrized using density-functional theory (DFT). The a-Si:H model employed in this work was originally developed by Guttman and Fong.[12] The realism is verified by bond length and RDF.

The RDF choice is true also for other disordered structures, as shown by Monaco *et al.*[13] in experimental studies of the effects of densification on the vibrational dynamics of $Na_2FeSi_3O_8$ glass and by Masciovecchio *et al.*[14] in experimental studies of SiO_2. Munejiri *et al.*[15] present first-principles molecular-dynamics simulations of liquid Ge and use RDF as a validation parameter. Akola and Jones[16] use combined density-functional/molecular-dynamics simulation to study liquid and amorphous structures of $Ge_{0.15}Te_{0.85}$, and GeTe alloys. Again, they use RDF as the link to the experimental results. Finally, Urli *et al.*[17] use tight-binding MD to study point defects in pure amorphous silica. It is interesting to note that the same authors state "…the atomic structure of these (amorphous) materials has not yet been completely resolved and the analogy with the continuous random network has not been fully established. In particular, there exists no evidence that the coordination number of the prototypical a-Si is equal to four, even though computer models do indicate that this might very well be the case; experiment has not yet been able to provide a definite answer to this question…."

It is evident from the above that agreement of the radial distribution function continues to be the "standard" protocol for judging the correctness of models of disordered materials. However, experimental measurements of RDF are not common and are difficult to implement; furthermore, no recent and accurate experimental data are available for a-Si:H. If the goal of future work in the field is to expand the investigation of the properties of disordered materials by examining more complex processes and characteristics such as the Staebler-Wronski effect, the density of states, atom migration dynamics, optical absorption, conduction, etc., then one must ask the question whether these properties are being examined within a realistic structure. What defines a realistic structure? Although agreement with the RDF is a necessary requirement, is this protocol sufficient for the validation of a model?

In contrast to RDF measurements, vibrational experiments are essentially more common, accurate, and, most notably, linked to various processes in disordered materials.[18,19] Therefore, apart from providing a useful means to access microscopic properties of noncrystalline materials, the verification of the validity of theoretical models can be based on calculated vibrational spectra. However, there is no satisfactory theoretical formalism available to decode vibrational spectra in terms of atomic-level processes within noncrystalline materials. Standard theoretical vibrational techniques (see, Ref. 20 and references therein) are not efficient for noncrystalline network due to lack of translational symmetry and complicated atomic dynamics.

To overcome these problems, the authors have developed a comprehensive approach that combines *ab initio* molecular dynamics and improved signal processing, which has proven to be a powerful tool for the determination of a number of fundamental properties of *a*-Si:H.[21,22] This paper, by further developing the above numerical methods, addresses a fundamental issue of verification of model validity in general by focusing on the correlation of noncrystalline material structures with vibrational properties and microscopic bonding. Using *a*-Si:H as an example, we were able to clearly separate all vibrational modes of the Si-H complexes and their *real time* genesis and uncover various types of *a*-Si:H instabilities. In particular, we have observed and correlated the signals at 2000 and 2100 cm^{-1} with their respective bond types, monohydrides, and dihydrides, respectively.[10] Other characteristic frequencies, observed experimentally, have also been reproduced and correlated with their appropriate bonding structures.

II. METHODOLOGY

A variety of numerical samples using a 64 Si atom supercell with a wide range of hydrogen concentrations was simulated by AIMD and visualized atom dynamics was used to extract *a*-Si:H frequencies by the signal-analysis method MUSIC.[23] We have found that, however, the vibrational spectrum of the amorphous 64 Si supercell with H atoms was practically impossible to analyze due to the excessive number of frequencies (compared, e.g., to the crystalline Si). Most importantly, hydrogen and silicon diffusions as well as H-bond switching modify the atomic vibrations during the long MD run, thus further complicating vibrational analysis. To overcome this difficulty, we have developed and extensively tested an approach that combines the signal analysis method MUSIC and the Fourier transform.[21] Finally, to get a deeper insight into the relations between vibrational and structural properties, we developed and applied the frequency-extraction method that follows real-time dependence of the vibrational spectra. We apply this method to track structural modification and rebonding of *a*-Si:H during a variety of thermal treatments. The remarkable advantage of this method is that it allows analyzing any set of molecular-dynamics data in terms of possible instability or even phase transition. In order to test the significance of a realistic reproduction of the RDF, in contrast to Ref. 21 we focused only on one hydrogen concentration, considering instead a few different sample-preparation procedures. We started with a crystalline silicon-cubic supercell, containing 64 Si and 8 H atoms (we verified that using a 128 Si supercell no significant difference was observed with respect to the 64 Si supercell). The system was melted at 3000 K. After its equilibration in the molten state for 5 ps using the Nosé thermostat, three different samples were created in the following ways: (a) the system was slowly cooled down to room temperature (RT) with cooling rate of 4.5×10^{14} K/s and then relaxed to zero temperature (sample a); (b) the system was rapidly quenched to zero temperature (sample b); (c) the system was kept in the molten state for an additional 2 ps, and then quenched to zero temperature as well (sample c). Next, the atoms in all three systems were slightly distorted from their equilibrium positions in order to perform RT MD runs for 10 ps to collect statistical data for vibrational analysis. The Nosé thermostat was off for the RT runs. It should be noted that samples (b) and (c) were obtained with a procedure nonconducive to a realistic structure obtained experimentally.

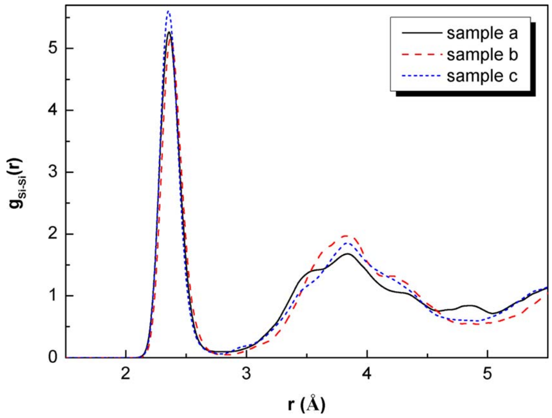

FIG. 1. (Color online) Radial distribution function for three samples prepared by three different methods from the same original (64 Si+8 H) supercell.

These three different numerical samples were analyzed in detail from the dynamical (vibrational frequencies and their real-time evolution) and statistical (various distribution functions) points of view. Calculated electronic and optical properties of the *a*-Si:H systems under consideration, including the density of states and dielectric function, have been analyzed by Kupchak *et al.*[22,24]

III. RESULTS

In Fig. 1 we show the RDF for all three samples; strikingly there is very little variation among the three spectra. Moreover, RDF does not demonstrate features that can be interpreted in terms of microscopic processes in the system. However, when we compare the vibrational spectra for the same three cases (see Fig. 2), there is a dramatic difference between sample (a) (the "realistic" *a*-Si:H structure, as indicated by the strong signal at ~2000 cm^{-1}, the characteristic monohydride stretching mode), and samples (b) and (c), where the location and/or intensity of the various peaks do not reproduce the standard experimental observations.[18,19]

Figures 3 and 4 show the RDF of the H-H pairs and the average bond-angle distribution for the three cases, clearly indicating a structural difference among the three samples. Indeed, it is crucial that not only the underlying silicon network follow the amorphous structure but also that the H

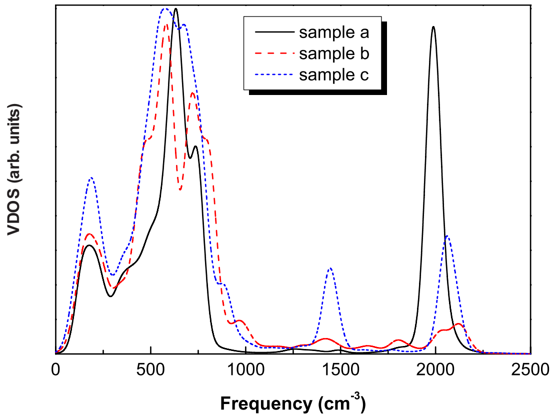

FIG. 2. (Color online) Vibrational density of states (VDOS) for the same three cases shown in Fig. 1. Note the essential modification of the spectra for the "unphysical" (b) and (c) samples.

atoms be embedded in the proper way within the silicon matrix. For instance, Tuttle and Adams[7] show that the energetics and properties of H atoms must be analyzed considering also their phases, i.e., dilute or clustered. It appears that the relative ratio of these phases and their distribution has an important role in determining the properties of *a*-Si:H.[7] This is a fundamental fact that needs to be taken into account, if the model has to be used to simulate processes connected with hydrogen dynamics, including the testing of some important models that have recently come to prominence as explanations of the Staebler-Wronski effect such as the floating-bond model[25] and the hydrogen-collision model.[26]

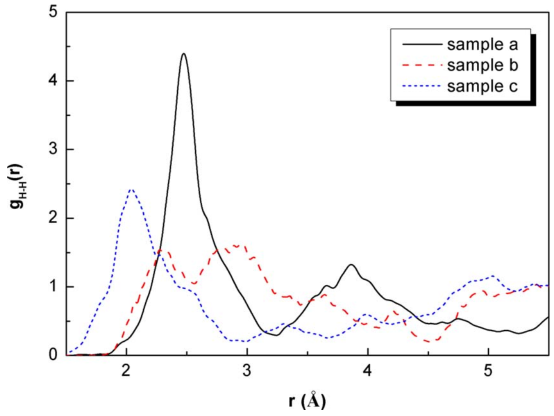

FIG. 3. (Color online) Radial distribution function for the H-H pairs for the three samples described in the text. Note the essential change in the distribution function due to difference in structure and bonding.

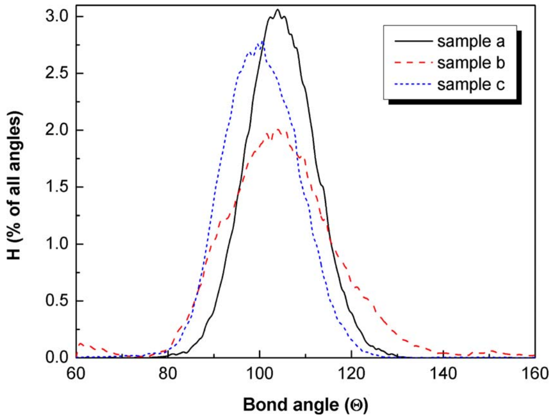

FIG. 4. (Color online) Variations in the average bond angle for H atoms for the same three *a*-Si:H samples as in the previous figures. The difference in the angle distribution is more pronounced than in the case of RDF.

The stability of the bonds is also important to verify the accuracy and validity of a model. Figures 5(a)–5(c) show the intensity of the various characteristic vibrational frequencies in *a*-Si:H as a function of time for the three samples, as produced by our modified signal-processing technique. The lighter color indicates a higher intensity, that is, the white region is where the peak is located. It is clear that we observe a stable bond only in case a: the only fluctuations we observe for this case is in the intensity of the peak; however, both the 2000 and 600 cm^{-1} features indicate very little shifts in the frequency position and a narrow peak (shown by the "spread" around the peak position). Furthermore, a lower intensity in the peak at 2000 cm^{-1} corresponds to a higher intensity in the peak at 600 cm^{-1}, indicating that the fluctuations in peak intensities are due to an alternating predominance of the stretching modes vs the rocking/bending/scissors modes. On the other hand, both samples (b) and (c) show large fluctuations in peak intensity, position, and a large spread of the signal at 600 cm^{-1}.

A few different methods have been tried in the past to recreate a realistic *a*-Si:H, including removing Si atoms from a pure-amorphous silicon network and "adding" H atoms.[9,27] It is clear that, however, in order to extract the relevant macroscopic parameters correlated with an amorphous structure, great care must be taken to verify the validity of the model beyond just the standard RDF of the Si network.

To confirm this we have run an additional test starting with a 64-atom amorphous silicon sample with no hydrogen obtained from the melt by slow cooling down to room temperature. We then added two hydrogen atoms at random positions within the unit cell and the system was relaxed to zero temperature. These H atoms were placed in the vicinity of fourfold-coordinated Si atoms with all their bonds satisfied by other Si atoms so that the creation of "free" interstitial hydrogen atoms seemed plausible. However, during the relaxation at zero temperature, both hydrogen atoms developed monohydride bonds with the nearest Si atoms, leading to a significant system distortion in the region of the monohydrides.

Subsequently the atomic positions were slightly distorted from the relaxed positions, an MD run was performed at 300 K and statistical data were collected before annealing (ba). During the MD run, the system was stable—no essential changes occurred in the atomic structure. The system was then annealed at ~700 K. After annealing (aa), the system was relaxed to zero temperature again and an additional MD run was performed at 300 K to collect statistical data. During the annealing, one of the hydrogen atoms "jumped" to another Si atom, and this new monohydride bond remained

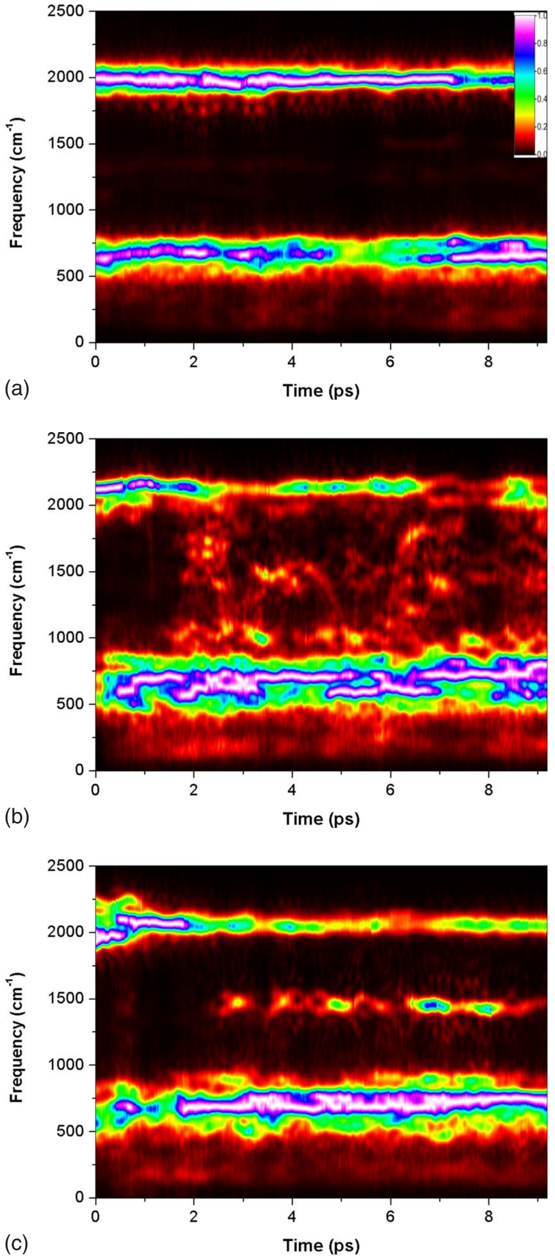

FIG. 5. (Color online) Real-time dependence of the vibrational frequencies for the three samples: (a) top, (b) middle, and (c) bottom. An intensity scale is shown in the inset on the graph for sample (a). Note the absence of the vibrations between two main low- and high-frequency modes in (a), and significant frequency instability for the samples (b) and (c).

stable for the rest of the simulation. Moreover, the "old" Si atom restored its bond with the nearest Si atom, which had been replaced by a monohydride before. The observations indicate essential structure and local bonding modification, and to quantify this we extracted the RDF and the vibrational spectra before (ba) and after (aa) annealing. These spectra are shown in Figs. 6 and 7. Once again, very little difference is observed between the two RDF spectra while the vibrational spectra clearly indicate that only after annealing were we able to achieve a realistic *a*-Si:H sample.

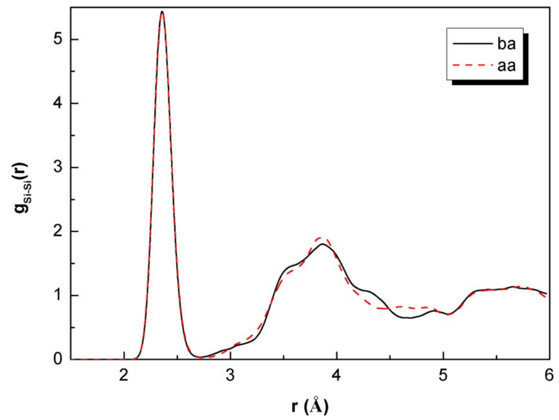

FIG. 6. (Color online) Radial distribution function for a test 64 (Si)+2 (H) system (there are two different structures but one system) before annealing (ba) and after annealing (aa). As for the case shown in Fig. 1, there are no noticeable differences in the RDF.

As well, we have compared a variety of *a*-Si:H samples with H content from 0% to 20% in Ref. 21 and we have found that the RDF practically does not depend on the amount of hydrogen in the sample. Furthermore, all the calculated RDF agree reasonably well with the most recent and accurate RDF measurement for *a*-Si with no hydrogen.[28] This reflects the fact that the most probable distance between neighboring atoms is equal to a sum of the atoms' covalent radii. Even when hydrogen passivates the dangling bonds, this does not modify the Si-Si bond length. On the other hand, atomic vibrations do depend on microscopic bonding (bonds), their angular distribution, distortion, or breaking. In fact, the experimental measurements[18,19,29] demonstrate a variety of spectral features that obviously require microscopic theoretical interpretation.

In order to further verify the validity of our model, we have studied the special case of metastable Si-H-Si bonds. Darwich *et al.*,[29] using infrared transmission spectroscopy (IRT) and infrared ellipsometry, observed a new metastable feature at ~1730 cm^{-1} during light soaking, which they attributed to a three center Si-H-Si bond (TCB). The authors remark that the theoretical calculation for the IRT frequency

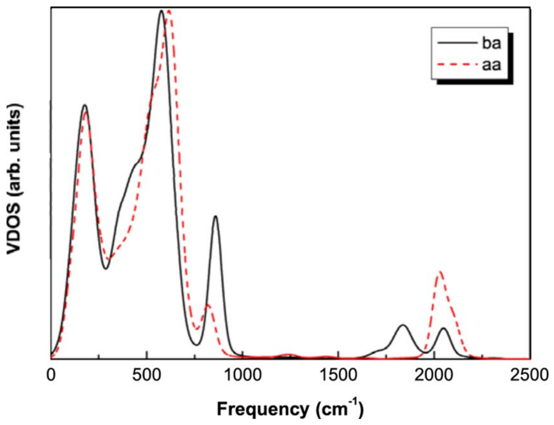

FIG. 7. (Color online) Vibrational density of states for the 64 (Si)+2 (H) system before annealing (ba) and after annealing (aa).

of such a complex had been a controversial issue, with the expected values located between 800 and 1950 cm^{-1}, and proposed that in fact the band at 1730 cm^{-1} represents the stretching mode of the TCB. From our simulations, we observe such a feature associated with a TCB type of bond between 1500 and 1800 cm^{-1}.[21]

This behavior was also observed by Su and Pantelides[9] at high temperatures. The authors used AIMD to simulate the hydrogen-migration process in a-Si:H. Their simulations were performed only at high temperatures (600–900 °C) with a supercell of 64 silicon plus only two hydrogen atoms. The RDF was used to verify the agreement with experimental data. A typical occurrence observed by the above mentioned authors is the migration of a hydrogen atom from a silicon atom (A) to another silicon atom (B) with a calculated frequency between 2000 and 2100 cm^{-1}. These, however, are the characteristic frequencies of stable monohydride or dihydride bonds rather than a metastable hydrogen bond.

Our AIMD results confirm Darwich's claim within experimental error. The decrease in the vibrational frequency with respect to that of a stable monohydride bond is due to the sharing of the hydrogen-electron density between two Si atoms. This decreases the Si-H bond strength, increases the bond length, and results in reduction in the vibrational frequency. Therefore, the band in the 1500–1800 cm^{-1} region can be interpreted as the signature of hydrogen metastable bonds, including the TCB bond, with variations in the frequency due to the different overlap between the H and the Si electron wave functions.

On the other hand, Tuttle and Adams[7] were able to reproduce a similar signal using DFT-based tight-binding MD but argue that the peak is due to a hydrogen atom bonded to an overcoordinated Si atom. They base this conclusion on tight-binding calculations that place the TCB in crystalline silicon at 1900–2000 cm^{-1}. However, as indicated by Darwich, other studies go as low as 800 cm^{-1} as a theoretical value for the peak. It should also be mentioned that, in the paper by Tuttle and Adams, there is a very strong signal at about 810 cm^{-1}, usually correlated with dihydride scissors/rocking modes. This signal however is much bigger than the corresponding stretching mode, which is not consistent with literature data. It should also be noted that the stretching mode shows a peaked tail above 1600 cm^{-1}, suggesting that the vibrational modes in this region might be caused by more than one H-bonding configuration. Additionally, the numerical sample preparation is not clearly described in Ref. 7; one possibility is that their configuration has been created "manually." In the current and our other related publications[21,22] we have used numerical amorphous samples that have been obtained in a "natural" way by slow cooling. Since we were able to reproduce all previously experimentally suggested Si-H complexes and even the H_2 "molecule" inside the amorphous network, we conclude that our results are essentially closer to the experimentally observed systems. Finally, the absence of translational symmetry and the presence of nonsaturated Si bonds, hydrogen switching between host Si atoms, and significant bond anharmonicity and diffusion make first-principles or *ab initio* molecular dynamics, as used in our work, a more accurate approach to modeling-hydrogenated amorphous Si than the tight-binding method used by Tuttle and Adams.

IV. CONCLUSIONS

Ab initio molecular dynamics is a powerful tool for the modeling of complex systems such as solid-state amorphous structures and it is being used to probe fundamental properties and dynamics of disordered materials. However, in order to validate the simulation of complex structure, bonding, and diffusion, a protocol needs to be established for the verification of the realism of the simulated models. Using hydrogenated amorphous silicon as an example, we have unambiguously demonstrated that reproduction of the radial distribution function, used commonly in numerical simulations, is not sufficient and must be complemented with verification of other more complex macroscopic properties. By focusing on the vibrational modes of the amorphous system, we have proven that vibrational spectra represent a crucial testing tool for noncrystalline materials because of their complexity and sensitive link to structure and bonding configuration. Successful reproduction of all the experimentally observed vibrational features for a-Si:H proves the validity of our algorithm, and indicates that hydrogen structure and dynamics are extremely sensitive to the parameters of the model. In order to correctly apply a numerical model to extract such important macroscopic parameters as density of states, optical gaps, and migration dynamics, the accuracy should be verified first by the derivation of the standard vibrational modes and comparison with experimental observation.

ACKNOWLEDGMENTS

The research was supported by the Centre for Materials and Manufacturing/Ontario Centres of Excellence (OCE/CMM) "Sonus/PV Photovoltaic Highway Traffic Noise Barrier" project, Discovery Grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Shared Hierarchical Academic Research Computing Network (SHARCNET).

---

*Corresponding author; franco.gaspari@uoit.ca

[1] R. A. Street, *Hydrogenated Amorphous Silicon* (Cambridge University Press, Cambridge, UK, 1991).
[2] T. Searle, *Amorphous Silicon and its Alloys* (INSPEC, London, 1998), chaps. VI-VII, p. 271–337.
[3] J. Poortmans and V. Arkhipov, *Thin Film Solar Cells* (Wiley, New York, 2006), p. 471.
[4] M. Ishimaru, J. Appl. Phys. **91**, 686 (2002).
[5] S. Izumi, S. Hara, T. Kumagai, and S. Sakai, J. Cryst. Growth **274**, 47 (2005).
[6] R. Singh, S. Prakash, N. N. Shukla, and R. Prasad, Phys. Rev. B **70**, 115213 (2004).

[7] B. Tuttle and J. B. Adams, Phys. Rev. B **56**, 4565 (1997).

[8] F. Buda, G. L. Chiarotti, R. Car, and M. Parrinello, Phys. Rev. B **44**, 5908 (1991).

[9] Y. S. Su and S. T. Pantelides, Phys. Rev. Lett. **88**, 165503 (2002).

[10] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).

[11] B. R. Tuttle, Phys. Rev. Lett. **93**, 215504 (2004).

[12] L. Guttman and C. Y. Fong, Phys. Rev. B **26**, 6756 (1982).

[13] A. Monaco, A. I. Chumakov, G. Monaco, W. A. Crichton, A. Meyer, L. Comez, D. Fioretto, J. Korecki, and R. Ruffer, Phys. Rev. Lett. **97**, 135501 (2006).

[14] C. Masciovecchio, G. Baldi, S. Caponi, L. Comez, S. Di Fonzo, D. Fioretto, A. Fontana, A. Gessini, S. C. Santucci, F. Sette, G. Viliani, P. Vilmercati, and G. Ruocco, Phys. Rev. Lett. **97**, 035501 (2006).

[15] S. Munejiri, T. T. Masaki, T. Itami, F. Shimojo, and K. Hoshino, Phys. Rev. B **77**, 014206 (2008).

[16] J. Akola and R. O. Jones, Phys. Rev. Lett. **100**, 205502 (2008).

[17] X. Urli, C. L. Dias, L. J. Lewis, and S. Roorda, Phys. Rev. B **77**, 155204 (2008).

[18] G. Lucovsky, R. J. Nemanich, and J. C. Knights, Phys. Rev. B **19**, 2064 (1979).

[19] L. S. Sidhu, T. Kosteski, S. Zukotynski, and N. P. Kherani, J. Appl. Phys. **85**, 2574 (1999).

[20] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).

[21] I. M. Kupchak, F. Gaspari, A. I. Shkrebtii, and J. M. Perz, J. Appl. Phys. **103**, 123525 (2008).

[22] I. M. Kupchak, F. Gaspari, A. I. Shkrebtii, Z. Ibrahim, and A. Kazakevitch, in *Proceedings of 33rd IEEE Photovoltaic Specialists Conference*, San Diego, USA, May 11–16, 2008, p. 206.

[23] J. Kohanoff, Comput. Mater. Sci. **2**, 221 (1994).

[24] A. I. Shkrebtii, I. M. Kupchak, and F. Gaspari, in *Amorphous and Polycrystalline Thin-Film Silicon Science and Technology 2009*, MRS Spring Meeting, San Francisco, April 2009 (unpublished).

[25] R. Biswas and B. C. Pan, Sol. Energy Mater. Sol. Cells **78**, 447 (2003).

[26] H. M. Branz, S. Asher, H. Gleskova, and S. Wagner, Phys. Rev. B **59**, 5513 (1999).

[27] T. A. Abtew and D. A. Drabold, Phys. Rev. B **74**, 085201 (2006).

[28] M. Saito, Y. Okamoto, A. Oshiyama, and T. Akiyama, Physica B **273-274**, 196 (1999).

[29] R. Darwich, P. Roca, I. Cabarrocas, S. Vallon, R. Ossikovski, P. Morin, and K. Zellama, Philos. Mag. B **72**, 363 (1995).