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Large and realistic models of amorphous silicon

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ABSTRACT

Amorphous silicon (*a*-Si) models are analyzed for structural, electronic and vibrational characteristics. Several models of various sizes have been computationally fabricated for this analysis. It is shown that a recently developed structural modeling algorithm known as force-enhanced atomic refinement (FEAR) provides results in agreement with experimental neutron and X-ray diffraction data while producing a total energy below conventional schemes. We also show that a large model (~ 500 atoms) and a complete basis is necessary to properly describe vibrational and thermal properties. We compute the density for *a*-Si, and compare with experimental results.

1. Introduction

Amorphous silicon (*a*-Si) and its hydrogenated counterpart (*a*-Si:H) continue to play an important role in technological applications, such as thin-film transistors, active-matrix displays, image-sensor arrays, multijunction solar cells, multilayer color detectors, and thin-film position detectors [1]. While a number of traditional methods, based on Monte Carlo and molecular-dynamics simulations, were developed in the past decades by directly employing classical or quantum-mechanical force fields – from the event-based Wooten-Winer-Weaire (WWW) [2, 3] bond-switching algorithm and the activation-relaxation technique (ART) [4, 5] to the conventional melt-quench (MQ) molecular-dynamics simulations [6-11] – none of the methods utilize prior knowledge or experimental information in the simulation of atomistic models of complex materials. It is now widely accepted that dynamical methods perform rather poorly to generate high-quality (i.e., defect-free) continuous-random-network (CRN) models of amorphous silicon by producing too many coordination defects (e.g., 3- and 5-fold coordinated atoms) in the networks. While the WWW algorithm and the ART can satisfactorily address this problem by producing 100% defect-free CRN models of *a*-Si, a direct generalization of the WWW algorithm for multicomponent systems is highly nontrivial in the absence of sufficient information on the bonding environment of the atoms. Likewise, the ART requires a detailed knowledge of the local minima and the saddle points on a given potential-energy surface in order to determine suitable low-lying minima that correspond to defect-free CRN models of amorphous silicon. On the other hand, the availability of high-precision experimental data from diffraction, infrared (IR), and nuclear magnetic resonance (NMR) measurements provide unique opportunities to develop methods, based on information paradigm, where one can directly incorporate experimental data in simulation methodologies. The reverse Monte Carlo (RMC) method [12-15] is an archetypal example of this approach, where one attempts to determine the structure of complex disordered/amorphous solids by inverting experimental diffraction data. Despite its simplicity and elegance, the method produces unphysical structures using diffraction data only. While inclusion of appropriate geometrical/structural constraints can ameliorate the problem, the generation of high-quality models of *a*-Si, using constrained RMC simulations, has been proved to be a rather difficult optimization problem and satisfactory RMC models of *a*-Si have not been reported in the literature to our knowledge. The difficulty associated with the inversion of diffraction data using RMC simulations has led to the development of a number of hybrid approaches in the past decade [16, 17]. Hybrid approaches retain the spirit of the RMC philosophy as far as the use of experimental data in simulations is concerned but go beyond RMC by using an extended penalty function, which involves total energy and forces from appropriate classical/quantum-mechanical force fields, in addition to few structural or geometrical constraints. The experimentally constrained molecular relaxation [18, 19] (ECMR), the first-principle assisted structural solutions [20] (FPASS), and the recently developed force-enhanced atomic relaxation [21-24] (FEAR) are a few examples of hybrid approaches, which have successfully incorporated experimental information in atomistic simulations to determine structures consistent with both theory and experiments. Recently, the FEAR has been applied successfully to simulate amorphous carbon (*a*-C) [24]. This is particularly notable as the latter can exist in a

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variety of complex carbon bonding environment, which makes it very difficult to produce *a*-C from *ab initio* molecular-dynamics simulations due to the lack of *glassy* behavior and the WWW bond-switching algorithm in the absence of prior knowledge of the bonding states of C atoms in *a*-C (e.g., the ratio of sp^2- versus sp^3-bonded C atoms with a varying mass density). In this paper, we show that the information-based FEAR approach can be employed effectively to large-scale simulations of *a*-Si consisting of 1000 atoms. The resulting models have been found to exhibit superior structural, electronic, and vibrational properties of *a*-Si as far as the existing RMC and *ab initio* MD models are concerned in the literature.

The rest of the paper is as follows. In Section 2, we discuss the computational methodology associated with the generation of CRN models using the FEAR method. The is followed by the validation of the properties of the FEAR models with particular emphasis on the structural, electronic, vibrational, and thermal properties in Section 3. Section 4 presents the conclusions of our work.

2. Methodology and models

For this study, three model sizes (216, 512 and 1024 atoms) were implemented with FEAR and compared with experimental data. Several algorithms and codes were utilized for the preparation of the models; namely, FEAR [21-23], RMCProfile [27], SIESTA [28] and VASP [29-31].

A random starting structure was constructed for each of the models and was refined by fitting to the experimental pair correlation functions $g(r)$ and/or the static structure factor $S(q)$ by employing RMCProfile. The refined structure is relaxed using conjugate gradient (CG) in SIESTA. The relaxed-refined structure is then refined by RMCProfile. This cyclic process is repeated until convergence is achieved (in this work, each FEAR step is defined by ~ 100 RMC accepted moves followed by 1 CG step, and a total of 6,000 FEAR steps were sufficient for a reasonable model of a-Si). For completeness the converged structure is then fully relaxed by VASP (plane wave LDA).

The partial refinement steps in RMCProfile were carried out with a minimum distance between atoms of 2.10 Å and maximum move distance of 0.15 Å–0.35 Å. The partial relaxation steps utilized SIESTA with a single-ζ basis set, Harris functional at constant volume, exchange-correlation functional with local-density approximation (LDA), periodic boundary conditions and a single relaxation step. The final relaxation step employed VASP with a plane-wave basis set, plane-wave cutoff of 350–450 eV, energy difference criteria of $10^{-4} - 10^{-5}$. The fully relaxed calculations were performed for $\Gamma(\vec{k} = 0)$. For all the FEAR models, we have used structure factor data from Laaziri et al. [25] for RMC refinement.

The three FEAR models and 216 MQ model have a number density of about 0.05005 atoms /Å^3, which is associated with atomic density of 2.33 g/cm^3 (for details Table 1). The 216 MQ model was fabricated by taking a set of random coordinates and equilibrating these coordinates at 3000 K for 6 ps, followed by cooling from 3000 K to 300 K within 9 ps, then equilibration at 300 K for 4.5 ps, and a full relaxation at 300 K. The MQ calculations were performed with a step size of 1.5 fs. These are typical simulation times used to prepare accurate *ab initio* models for *a*-Si.[1]

We have also considered two large (4096 atoms and 10,000 atoms) WWW [2, 3] models in our comparison. These two WWW models were relaxed using SIESTA with a single-ζ basis set, LDA at constant volume utilizing Harris functional.[2]

[1] It is worth noting that MQ is not a unique process, and it has recently been shown that very slow quenches of liquid silicon can lead to models approaching WWW quality, contrary to the conventional view that MQ only works for glass formers. These are very extended simulations however, and do not seem to be a very efficient way (FEAR is an efficient method, and the models reported here required only 6,000 force calls) to model non-glass forming materials [32-34].

3. Results

3.1. Structural properties

A comparison of structure factors for the six models 216 MQ, 216 FEAR, 512 FEAR, 1024 FEAR, 4096 WWW and 10,000 WWW models with respect to experiment [25, 26] is shown in Fig. 1. From, Fig. 1 (left panel) we can clearly observe that these models of up to 512 atoms is insufficient to resolve the first peak occurring at low q. In contrast, the 1024 FEAR model does well even in comparison to much larger models as seen in Fig. 1 (right panel). This is also indicated in the real space information $g(r)$ (Fig. 2), where we observe that 10,000 WWW model is slightly shifted as compared to the experiment [25] for the first and second neighbors peak. We report the details of our simulation and important observables in Table 1.

From Table 1, we observe that there are some defects in our models. These structural defects arise due to a small fraction (~ 5%) of over co-ordinated and under co-ordinated atoms. This explains the fact that all of our models have coordination value slightly above perfect four-fold coordination. Experimentally, it is also observed that *a*-Si does not posses a perfect four fold coordination [25, 26]. Our final models obtained after relaxation attain energies (eV/atom) equal or less than models obtained from MQ.

We further show our plots of bond-angle distribution in Fig. 2 (right panel) to attest accuracy of FEAR models. As seen in Fig. 2 the peak of the bond angle is close to the value of tetrahedral angle 109.47 °. Similarly, from ring statistics (Fig. 3) we observe that these a-Si networks mostly prefer a ring size of 5, 6, 7. Small rings (mostly 3-membered rings) are responsible for a unrealistic peak seen in unconstrained RMC [21] at an angle around ~60°. Opletal et al. have proposed use of a constraint for removal of these highly constrained 3 membered rings in their several works [16, 35]. FEAR method which incorporates accurate *ab initio* interaction enables us to remove these high energy structures without satisfying an extra criterion.

3.2. Electronic properties

Electronic properties such as electronic density of states (EDOS) reveal crucial information regarding accuracy of models. In particular, Prasai et. al. and others [38, 39] have used electronic information to aid in modeling amorphous system. Conversely, EDOS obtained for our models validate accuracy of our models. We have shown our plot of four models in Fig. 4. We have also studied the localization of electronic states by plotting inverse participation ratio (IPR) in conjunction with EDOS. We observe both plots with same qualitative resemblance with few localized states appearing near the Fermi energy ($E_F = 0$). These localized states arise due to the defects in the model (3-fold and 5-fold atoms).

We compare our large model of 4096 atoms along with our FEAR models. Due to gigantic size of this model, we have used Harris Functional and single-ζ basis set to evaluate the electronic density of states of these models. To our knowledge this is first time reporting of an *ab initio* based EDOS of *a*-Si models this big. Drabold et al. have previously carried out an extensive research regarding the exponential tail (valance and conduction) observed in amorphous silicon [40-42]. We report our result of EDOS for these models in Fig. 5. We observe that a 216 atom model gives us a very crude representation of these tails (valance and conduction). Meanwhile, FEAR models 512 and 1024 compare well with the large WWW models. Fedders et al. [43] have revealed that the valance tail prefers short bonds while the conduction tail prefers long bonds.

[2] We minimized our 4096 WWW model to a have forces less than 0.01 eV/ Å and for the 10,000 WWW model after ~ 100 CG steps, RMS force of 0.024 eV/ Å was obtained.