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Atomistic simulation of nearly defect-free models of amorphous silicon: An information-based approach

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ABSTRACT

We present an information-based total-energy optimization method to produce nearly defect-free structural models of amorphous silicon. Using geometrical, structural, and topological information from disordered tetrahedral networks, we have shown that it is possible to generate structural configurations of amorphous silicon, which are superior than the models obtained from conventional reverse Monte Carlo and molecular dynamics simulations. The new data-driven hybrid approach presented here is capable of producing atomistic models with structural and electronic properties which are on a par with those obtained from the modified Wooten-Winer-Weaire (WWW) models of amorphous silicon. Structural, electronic, and thermodynamic properties of the hybrid models are compared with the best dynamical models obtained from using machine-intelligence-based algorithms and efficient classical molecular dynamics simulations, reported in the recent literature. We have shown that, together with the WWW models, our hybrid models represent one of the best structural models so far produced by total-energy-based Monte Carlo methods in conjunction with experimental diffraction data.

INTRODUCTION

Amorphous silicon continues to play a major role in the application of silicon-based device technology [1]. Recent developments of silicon-based heterojunction intrinsic technology (HIT) [2] for photovoltaic cells and the two-qubit quantum logic gates [3] are indicative of the continuing importance of amorphous/crystalline silicon and silicon-based materials. While the structure of amorphous silicon (*a*-Si) can be readily characterized by a continuous random network (CRN) [4], which is characterized by the

presence of high degree of tetrahedral ordering, the construction of a CRN model with minimal strain and few coordination defects has been a vexing problem in structural modeling of amorphous silicon. Until very recently, high-quality structural models of *a*-Si are best produced by the Monte Carlo based bond-switching algorithm of Wooten, Winer, and Weaire (WWW) [5]. The subsequent modification of the algorithm by Barkema and Mousseau [6] further augments the capability of the WWW method in producing large structural models of *a*-Si, exhibiting experimentally compliant structural, electronic, and vibrational properties. Other important approaches that are often followed to simulate *a*-Si are molecular dynamics (MD) simulations [7–10] (either *ab initio*/classical MD or an intermediate approach between the two), reverse Monte Carlo simulations (RMC) [11–13], and the recently developed hybrid RMC methods in various flavors [14–16] including the Force Enhanced Atomic Refinement (FEAR) approach [15]. In the following, we present an information-driven inverse approach (INDIA) [17], where we have shown that high-quality structural models of amorphous silicon can be produced efficiently by inverting experimental structure-factor or pair-correlation data along with additional geometrical and topological information on the local bonding environment of the silicon atoms in the amorphous state.

COMPUTATIONAL METHOD

Recently, we have implemented an information-driven inverse approach (INDIA) to model the atomistic structure of *a*-Si. A detailed description of the method can be found in Ref. [17]. We have shown that structural models can be generated by inverting a set of experimental diffraction data and structural constraints in conjunction with an appropriate total-energy functional. Here, we briefly illustrate the method by employing the modified Stillinger-Weber (SW) potential [18,19] to describe the interaction between Si atoms, which can be defined as,

$$V(R^N) = \frac{1}{2}\sum_{i=i}^{N}\sum_{\substack{j=1\\(j\neq i)}}^{N} v_2(r_{ij}) + \sum_{i=1}^{N}\sum_{\substack{j=i\\(j\neq i)}}^{N}\sum_{\substack{k=1\\(k\neq i)\\(k\neq j)}}^{N} v_3(\boldsymbol{r}_{ij},\boldsymbol{r}_{ik}), \tag{1}$$

where the two-body contribution, $v_2(r_{ij})$ to the potential energy is given by,

$$v_2(r_{ij}) = \epsilon A\left[B\left(\frac{r_{ij}}{\sigma}\right)^{-p} - 1\right] exp\left(\frac{\sigma}{r_{ij}-a\sigma}\right)\Theta(a\sigma - r_{ij}), \tag{2}$$

and $v_3(\boldsymbol{r}_{ij},\boldsymbol{r}_{ik})$ is the three-body contribution to the potential energy,

$$v_3(\boldsymbol{r}_{ij},\boldsymbol{r}_{ik}) = \epsilon\lambda\left(\cos\theta_{jik} + \frac{1}{3}\right)^2 exp\left(\frac{\sigma\,\gamma}{r_{ij}-a\sigma} + \frac{\sigma\,\gamma}{r_{ik}-a\sigma}\right) \times \Theta(a\sigma - r_{ij})\Theta(a\sigma - r_{ik}), \tag{3}$$

with Θ being the Heaviside step function. The potential parameters, due to Vink et al. [19], were used in this work. The simulations were carried out by maintaining a minimum distance of 2.0 Å between the silicon atoms and the mass density of the model matched with the experimental density of *a*-Si of 2.25 g/cm^3. The electronic and vibrational properties of models were studied using the local-basis density-functional theory (DFT) code SIESTA [20]. The latter employs pseudoatomic orbitals as basis functions (double-zeta basis in the present work) and norm-conserving Troullier-Martins pseudopotentials [21] within the Perdew-Burke-Ernzerhof (PBE) formulation [22] of the generalized gradient approximation (GGA).

RESULTS AND DISCUSSION

In this section, we discussed the results from INDIA models for amorphous silicon and compared our results with the corresponding WWW models. In addition, we have also compared the results with the best molecular-dynamical models obtained from using machine-intelligence-based algorithms (ML-MD) [7] and molecular dynamics simulations (SW-MD) [8]. We have studied the structural properties of *a*-Si models consisting of up to 1024 atoms and presented the results in Table I, which lists various structural properties of relaxation-based INDIA and WWW models, and MD-based SW models showing the average bond length ($\langle r \rangle$), average bond angle ($\langle \theta \rangle$), and the percentage of 4-fold coordination number (C_4), as well as the effective coordination number (ECN). We have computed $\langle r \rangle$ and ECN using the relations described in Ref. [23,24].

Table I. Structural properties of INDIA, SW-MD, and WWW models: average bond length $\langle r \rangle$, average bond angle $\langle \theta \rangle$, the root-mean-square (RMS) deviation on bond angle $\Delta\theta$, percentage of 4-fold coordination number C_4 and the ECN, respectively.

Model	N	$\langle r \rangle$	$\langle \theta \rangle$	$\Delta\theta$	$(\Delta\theta_G)^a$	C4 (%)	ECN
INDIA	300	2.386	109.10	11.41	10.42	99.33	3.956
SW-MD		3.380	109.22	9.31	8.44	99.33	3.973
WWW		2.378	109.18	10.44	10.13	100.0	3.963
INDIA	512	2.387	109.10	11.48	10.64	99.60	3.955
SW-MD		2.379	109.27	9.12	8.58	99.22	3.976
ML-MD [b]		2.371	109.19	9.69	9.36	98.44	3.940
WWW		2.365	109.11	10.69	10.47	100.0	3.974
INDIA	1024	2.390	109.01	11.96	10.78	98.34	3.958
SW-MD		2.381	109.27	8.94	8.46	99.22	3.968
WWW		2.371	109.14	10.63	10.30	100.0	3.969

[a] *Values from a Gaussian approximation;* [b] *From Ref. [7]*

We have compared the static structure-factor S(k) for the INDIA models with the WWW models and the experimental structural-factor data from Laaziri et al. [25]. The S(k) in Fig. 1(a) shows that the INDIA models agree with the WWW models, as far as the two-body correlations are concerned and the results agree well with the experimental data for as-deposited *a*-Si samples from Laaziri et al. [25]. Secondly, we have computed the Voronoi-volume of the 512-atom INDIA, WWW, and SW-MD models and shown the Voronoi-volume distribution in Fig. 1 (b). It is apparent from the latter that, as far as the Voronoi volumes or the interstitial regions of the atoms are concerned, the SW-MD models are more ordered than the corresponding WWW and INDIA models. This observation is consistent with the fact that MD models generally more closely represent annealed samples of *a*-Si than those obtained from the relaxation-based Monte Carlo or similar approaches.

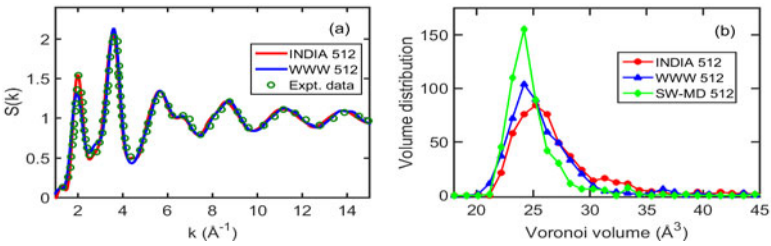

Figure 1. (a) Structure-factor, S(k), from the 512-atom INDIA and WWW models compared with the experimental data for as-deposited *a*-Si samples from Laaziri et al. [25], reprinted with permission from American Physical Society. (b) The (approximate) distributions of Voronoi volumes obtained from the INDIA, WWW, and SW-MD models.

Since the bond angles between the nearest-neighbor atoms characterize a three-dimensional distribution of the atoms in real space, we analyze the bond-angle distribution (BAD) of the atoms in the networks. The distribution is found to be essentially Gaussian in nature, which gives the average bond angle close to the value of ideally tetrahedral-bonded silicon atoms of 109.47° in crystalline silicon and the root-mean-square (RMS) deviation of the bond angles ($\Delta\theta$) in the experimentally observed range of 9-11° [26]. To obtain $\Delta\theta$, we fitted the BAD with a Gaussian distribution. Although the Gaussian approximation to the shape of the bond-angle distribution somewhat underestimates the RMS value, due to the absence of a few large/small angles in the distribution, it describes the BAD fairly accurately for high-quality *a*-Si networks. This is reflected in Table I.

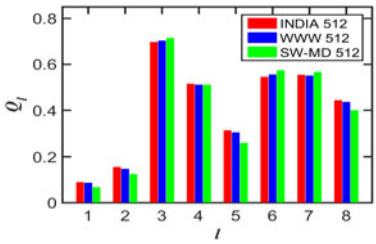

Figure 2. Distribution of the bond-orientational parameter, Q_l, for the 512-atom INDIA, WWW, and SW-MD models. See text for the discussion.

Further characterization of the network is possible by examining the bond-orientational order parameter (BOP), Q_l, as defined by Steinhardt et al. [27], which provides information on the orientation of a group of bonds. Figure 2 shows the Q_l values, for l = 1 to 8, for INDIA, WWW, and SW-MD models consisting of 512 atoms. The BOP not only incorporates some aspects of structural information from higher-order correlation functions, but also provides a simple and effective measure for determining the presence of microcrystalline or paracrystalline structural units in the networks [28]. Here, we have used $Q_l(l = 1,2,5)$ to determine the *degree of crystallinity*. While the magnitude of Q_1, Q_2, and Q_5 are exactly zero for ideal *c*-Si [8], a high value of Q_5 for the INDIA and WWW models indicates more amorphous or disordered nature of these models in comparison to the SW-MD model.

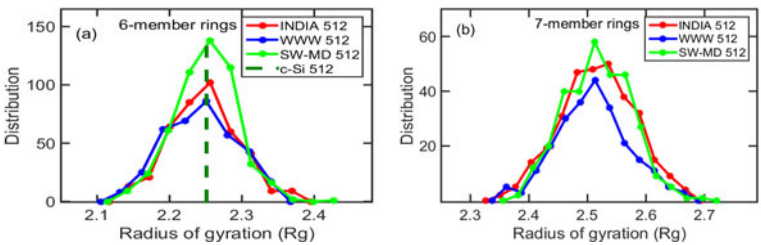

Figure 3. The distribution of the radii of gyration of (a) 6-member rings and (b) 7-member rings for the 512-atom INDIA, WWW, and SW-MD models of *a*-Si. The R_g of *c*-Si for 6-member rings is indicated by a vertical dashed line in Fig 3(a).

We have also examined the topological connectivity and the associated length scale for various ring structures present in the amorphous networks by computing the radius of gyration (R_g) of the rings. The R_g values and the numbers of the high-member rings (>= 7-member) can be indicative of the presence of intermediate range order (IRO)

in amorphous networks. The distributions of R_g of 6-member rings and 7-member rings are shown in Fig. 3(a) and Fig. 3(b) for the 512-atom models, respectively. The R_g plot in Fig. 3(a) indicates the presence of more 6-member rings in the SW-MD model compared to the INDIA and WWW models of an identical size. This can be attributed to the somewhat more ordered nature of the SW-MD model, which has been obtained from the MD simulations and thus can be compared with annealed samples of *a*-Si. The average R_g value of 6-member rings in *c*-Si is found to be 2.25 Å, which is somewhat lower that the average bond length (of 2.35 Å) in ideal *c*-Si, due to the non-planar nature of the hexagonal rings. Finally, we address the electronic and thermodynamic properties of the INDIA models. Toward this end, we plot the electronic density of states and the variation of the specific heat at constant volume with temperature. Figure 4(a) shows the density of electronic states for the 300- and 512-atom INDIA models and compared the results with the same from the 512-atom WWW model. The INDIA models produce a remarkably clean electronic gap, almost identical of the WWW model. We computed the specific heat (C_v) of the 300- and 512-atom INDIA models in the temperature range of 10 K – 300 K. The specific heat, C_v, was calculated from the (discrete) vibrational frequencies (ω) obtained from direct diagonalization of the dynamical matrices in the harmonic approximation using the relation [29],

$$C_v(T) = k_B \sum_{\boldsymbol{k},j} \frac{\left(\frac{\hbar\omega_j(\boldsymbol{k})}{2k_BT}\right)^2}{sinh^2\left(\frac{\hbar\omega_j(\boldsymbol{k})}{2k_BT}\right)} \qquad (4)$$

and compared with the experimental data obtained by Zink et al. [30] at low temperature in the range from 10 K to 300 K. Figure 4(b) shows the low-temperature dependence of the specific heat (C_v/T^3) with temperature from 10 K to 300 K. The result from Fig. 4(b) suggests that the INDIA models are in good agreement with the experimental data for T > 40 K. The inset shows the classical *Dulong-Petit* limit ($C_v = 3R$) as the temperature approaches to 300 K.

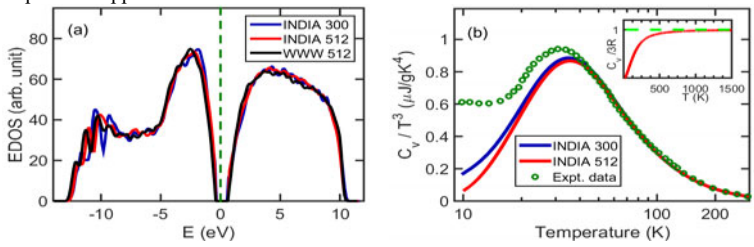

Figure 4. (a) The electronic densities of states of *a*-Si from 300-atom INDIA (blue), 512-atom INDIA (red), and WWW (black) models with the Fermi level indicated by a vertical green dashed line at 0 eV. (b) Low-temperature dependence of the specific heat of the 300- and 512-atom INDIA models compared with the experimental data (green) by Zink et al. [29], reprinted with permission from American Physical Society and the classical *Dulong-Petit* limit (shown as inset).

CONCLUSIONS

In this paper, we have studied the structural, electronic, and thermodynamic properties of amorphous silicon using an information-driven inverse approach developed in Ref. [17], which simultaneously uses experimental structure-factor and a few structural constraints along with a total-energy functional. By introducing a subspace

optimization scheme, we have shown that structural constraints can be readily incorporated to produce high-quality model configurations of *a*-Si, which are otherwise very difficult to achieve using the conventional RMC and hybrid RMC schemes. The resulting data-driven optimization method produces high-quality (i.e., a few coordination defects and a narrow bond-angle distribution) CRN models of amorphous silicon of size up to 1024 atoms. These relaxation-based models have the average bond angle of 109.2° and the root-mean-square (RMS) deviation of 9-11°, which are within the range of experimental value obtained from Raman measurements. This data-driven computational approach can produce realistic models of *a*-Si, which exhibit accurate realistic structural properties as produced by the WWW method. The INDIA models show not only an excellent agreement with structural properties but also able to produce a clean gap in the electronic density of states and the thermodynamic properties, compatible with experimental measurements.

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