A computational study of elastic properties of disordered systems with voids

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Abstract

We present a computational study of elastic properties of disordered systems with voids. The influence of hydrogen and voids on the elastic properties has been investigated by means of atomistic simulations using empirical potentials for hydrogenated amorphous silicon. The elastic constants have been obtained from the fluctuations of the simulation cell in Monte Carlo simulations at constant pressure and temperature. Our results indicate that the softening of the elastic constants of a-Si:H observed experimentally upon increasing hydrogen content cannot be explained by a weakening of the network induced by the reduced coordination but should be attributed instead to the formation of voids. A simple relation between Young's modulus and the density is presented.
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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has been over the last decades the focus of many experimental and theoretical investigations, motivated by technological applications as well as by fundamental interest [1,2]. The mechanical properties of a-Si:H are of particular relevance, especially in applications such as MEMS [3]. Yet, very little is known about the elastic properties of a-Si:H, and in particular about their relation to fundamental aspects such as the microscopic structure of the amorphous network [3–8]. Experimental results on the elasticity of a-Si:H [6–8] have reported a significant dependence of the elastic constants on the percentage of hydrogenation. However, no attempt has been made so far to connect these findings with the microscopic structure of the network. It has been recently pointed out that voids may play an important role in determining the microscopic properties of a-Si:H [9,10], and of other amorphous networks, however a quantitative study of their influence on the elastic properties is still lacking [7,3]. Computational approaches are in principle very valuable to explore such issues, because they allow the study of elasticity in direct connection to the microscopic structure. However, attempts to understand the elastic constants in amorphous silicon [3–5] have been restricted so far to pure a-Si and to the role of coordination defects. It was found that coordination defects do not affect the elastic properties of a-Si significantly and that the dependence follows the universal behaviour observed for continuous random networks (CRN) [11,12]. Elasticity in real systems is likely to be heavily affected by residual dangling bonds, by voids, and, in the case of a-Si:H, also by hydrogenation, none of which is accounted for in the CRN model. This work aims at covering this gap by means of atomistic simulation of the elastic properties of systems with voids by exploring an explicit model of a-Si:H.

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2. Methodology

The model is generated from a fully tetrahedral continuous network with 216 silicon atoms generated with the Wooten–Winer–Weaire (WWW) scheme (Djordjević–Thorpe–Wooten (DTW) model), with periodic boundary conditions [13,14]. Void-free hydrogenated models with various hydrogen concentrations were constructed by randomly adding protons in the DTW model and allowing for full structural relaxation. Models with voids were generated by removing selected Si atoms and by fully relaxing the structure. Hydrogenated samples with voids were generated by saturating with hydrogen, before relaxation, all dangling bonds at the void surface, and then by fully relaxing the atomic positions. Two different cases of void size distribution were considered: more than one small spherical void (with ∼5 Å of diameter) and a single cylindrical void (with diameter larger than 5 Å). For all cases, the elastic properties were averaged over at least three different configurations. Tests with pure crystalline Si and a-Si using smaller (64 atoms) and larger (1000 atoms) computational cells indicate that size effects are not significant for the investigated properties.

We have employed in our calculations the Tersoff model [15] to describe the atomic interactions between hydrogen and silicon atoms. This potential is known to describe reasonably well the elastic properties of crystalline and amorphous silicon. In order to check the effect of different potentials and their accuracy, we have also carried out calculations using the Environment Dependent Interatomic Potential (EDIP) model [16] for both crystalline and amorphous silicon without hydrogen. No parametrization for Hydrogen are available to EDIP model. Details for Tersoff and EDIP potentials can be found in Refs. [15,16], respectively.

Elastic constants, Young's modulus and Poisson's ratio were directly obtained from Monte Carlo (MC) simulations by analyzing the box side fluctuations in the NPT ensemble, with variable box shape. The method is an extension of the original idea of Parrinello and Rahman of averaging strain fluctuations [17,18]. The version of the method used here is described in Refs. [19–22].

The MC method was implemented using the Metropolis algorithm. Two kinds of trial moves were used. The first one concerned changes of the atom positions. The second kind of moves corresponded to changes of the components of the symmetric box matrix. Typical lengths of the runs were of about 5×10^6 trial steps per particle (MC cycles), after equilibration. Longer runs were performed to check the convergence of the method. The system was kept at zero external pressure and room temperature during the simulations.

3. Results and discussion

We first discuss the results of our simulations for pure a-Si, and compare them with the existing literature (Table 1).

Table 1
Theoretical and experimental data for the elastic constants (in GPa) of crystalline and amorphous silicon at 300 K

	c-Si			a-Si			
	expt. [23]	EDIP	Tersoff	expt. [24]	EDIP	Tersoff	TB [5]
C_{11}	165	166.7	139.5	156.0	134.3	149.6	149.0
C_{12}	64	70.8	73.8	57.8	87.9	66.8	46.9
C_{44}	79.2	67.9	67.1	49.2	23.5	39.0	55.4

In agreement with earlier studies, we find that the elastic moduli in the amorphous phase are smaller than those of the crystalline phase. Moreover, the results for model system of a-Si show a smaller deviation from the Cauchy relation. Among the two interatomic potentials used in this work, Tersoff and EDIP, the EDIP model provides better agreement with experimental data for the elastic constants of the crystalline phase. On the other hand, for the amorphous case, a closer agreement with experimental data is observed by using the Tersoff potential. Overall, our calculated elastic constants for model system of a-Si agree within a few percent with previous calculations using the same empirical potentials [3,4] and are in satisfactory agreement also with more accurate calculations based on the tight-binding (TB) approximation [5]. This indicates that the computational scheme used here is suitable for a semi-quantitative description of the elastic properties of crystalline and amorphous silicon.

We now discuss the effects of hydrogen content and voids on the elastic properties of our amorphous silicon model based on empirical potential. Several models of a-Si:H were constructed as described above, by varying density and hydrogen content separately. In Fig. 1 we report
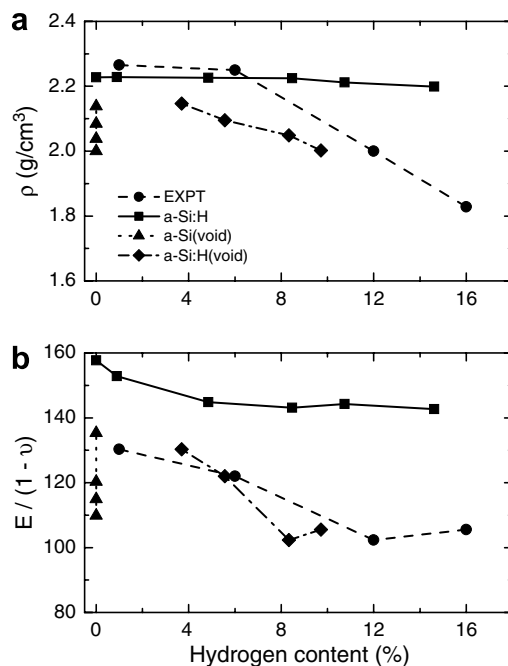

Fig. 1. Variation of the density (a) and biaxial modulus (b) of a-Si:H with hydrogen content. Filled circles are experimental data from reference [6]. All other data points are the results of our calculations.

the dependence of the calculated densities and elastic constants on hydrogen content. We find that in models without voids the density is basically independent of hydrogen concentration, while we observe a decrease of the density in models with voids. Experimental data on the density of a-Si:H show that its dependence on hydrogen content is weak for concentrations <6–8%, while density decreases significantly at higher concentrations. Therefore, our calculations suggest that in a-Si:H samples, hydrogen can be readily incorporated in the network only if its concentration is <6–8 %. At higher concentrations hydrogen appears to stabilize the formation of voids.

A similar behaviour is found for the dependence of the biaxial modulus (defined as $\frac{E}{1-v}$, where E is Young's modulus and v the Poisson ratio) on hydrogen content. The biaxial modulus of void-free samples is found to decrease slightly with increasing hydrogen content, see Fig. 1(b). We attribute such weakening to the fact that the formation of silicon-hydrogen bonds lowers the network connectivity and therefore reduces its rigidity. Samples with voids display a stronger decrease of the biaxial modulus with hydrogen content, i.e. with void volume. Interpretation of experimental data for the biaxial modulus is less obvious than in the case of density. However, if we accept the conclusion that real samples are void-free at low hydrogen concentrations, then it appears that a part from an overall scale factor, which can be attributed to the potential (see Table 1), the dependence of the experimental data is consistent with a mild decrease at low concentrations and with a steeper decrease at concentrations larger than 6–8%. It is interesting to remark that the calculated values of the biaxial modulus with voids are not affected by whether voids are passivated with hydrogen or not. In other words, while hydrogen appears to be responsible for the formation of voids at sufficiently high concentrations, its presence does not appear to influence the elastic properties directly.

This idea is illustrated and supported by the plot in Fig. 2, where we show the dependence of Young's modulus on the density, for all samples considered in this work. All results appear to lie on a s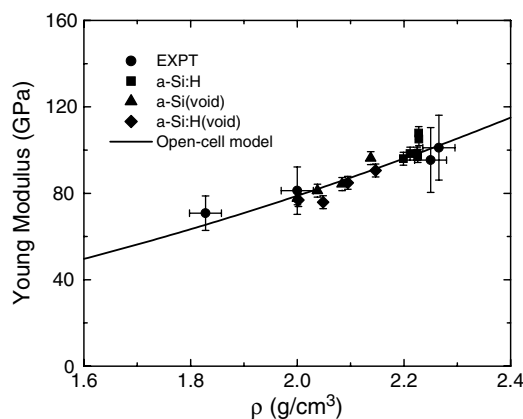ingle curve, regardless of their hydrogen content, indicating that elasticity is uniquely controlled by the voids. Universal models for the density dependence of Young's modulus in open structures have been already developed for cellular materials [25]. According to these models, Young's modulus (E) is related to the density (ρ) by the power law relation

$$\frac{E}{E_s} = C\left(\frac{\rho}{\rho_s}\right)^n \tag{1}$$

where E_s and ρ_s are Young's modulus and density of the constituent solid (bulk amorphous silicon). In our case, the best fit with the results of Fig. 2 is obtained for $C = 0.92$ and $n = 2.5$.

Whether such ideas can be extended to other amorphous networks, such as amorphous carbon and silica glass, remains to be seen.

4. Conclusions

In conclusion, our computational studies have uncovered interesting features concerning the elastic properties of systems with voids based on hydrogenated amorphous silicon within the Tersoff and EDIP models. First, this study shows that hydrogen incorporation in a-Si:H induces the formation of voids, for hydrogen contents larger than 6–8%. Moreover, we find that the significant departures of the elastic properties of a-Si:H from those of a-Si observed in experiments should be attributed to the appearance of voids, and not to a weakening of the network rigidity induced by the reduced coordination. Furthermore, a universal relation between Young's modulus and density has been found, which may be explained by using concepts of the theory of cellular solids.

Acknowledgements

Fig. 2. Behaviour of Young's modulus as a function of density. Legend same as Fig. 1.

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