Crystalline and amorphous nanostructures in porous silicon

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Abstract

We report ab initio molecular dynamic simulations of several supercells of crystalline porous silicon, that are first relaxed and then analyzed by their radial distribution functions (RDF). The porosities vary from 10% to 80% of the total volume of the supercell. The interatomic distance is determined by the position of the first peak of the RDF. We manipulated a maximum of 500 atoms of silicon and a minimum of 32. The interatomic distance of the model with a porosity of 10% was 2.35 Å, for those models with porosity from 11% to 50% was 2.45 Å and finally, 2.55 Å for those with a porosity greater than 50%. If the supercell backbone structure is small compared with the void of the supercell, then the interatomic distance between the silicon atoms run out of the crystalline value. Our results agree with experiment.

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1. Introduction

Silicon is an amazing element that can be used in nano-electronic devices [1] and in Si photonics as an integration platform [2]. At the nanometer scale, the size of the system becomes an important factor to obtain the correct system properties. That is why we consider this, as it is necessary to understand the relation between the size of the system and the changes in its structure and electronic properties, as the first step to investigate the influence of the topological arrangements in the atomic constituents of the models obtained in our porous silicon.

Porous silicon has been studied extensively, both experimentally and theoretically, due to the interesting luminous properties that it displays [3]. We present the radial distribution functions of different nanostructures of porous silicon and we point out the important role that the size of the system has on it is topological nature.

Simulationally, the pioneering ab initio Car–Parrinello (1985) molecular dynamics approach permeated the molecular dynamics procedure and its application to complex systems in the literature, and inspired advances in the DFT theory and molecular dynamics. One of the more interesting advances was the Lin and Harris method [4] that we use for our simulation.

Previous works on ab initio simulations have calculated the radial distribution function for the amorphous silicon [5] and for amorphous porous silicon [6]. In addition, the radial distribution function of the crystalline silicon is well known. The positions of the first peak of these curves will be used as a point of reference to determine the topological nature of our simulated structures.

2. Method

We generate several porous silicon supercells by replicating the silicon crystalline unit cell a desired number of times along each axis. At this stage, the supercells contain at least 64 silicon atoms and a maximum of 1000. The second step is to carve a pore in the supercell fixing at the same time the porosity of the model. The porosity is given as the ratio

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of the number of atoms removed over the total number of atoms initially in the supercell; i.e. as the ratio of the corresponding densities. We separated the supercells generated in two groups: the first group concerns the models with a porosity from 10% to 80%, a pore with no special direction and with a fixed volume of the supercell (fixed length of the supercell side), on the other hand the second group contains the models with a fixed porosity of 50%, a pore along the Z axis and with varying volume supercells (variable length of the supercell side). For both groups a lot of non-bonded atoms appear and the structure is quite 'artificial' since they are not at their energy minima; because of this we decided to relax them. After relaxation, some of the silicon atoms that were not bonded became bonded and the shape and size of the pore in the supercell changed.

We then obtained the radial distribution functions (RDFs) for both groups of models, and the position of the first peak of this curve is considered as the average interatomic distance between nearest-neighbor (nn) silicon atoms. For the second group of models we compared the nn interatomic distance of the silicon atoms lying on the pore surface to the nn interatomic distance of the rest of the silicon atoms.

We use FASTSTRUCTURE [7], a DFT code based on the Harris functional [8], to allow a molecular dynamics relaxation. We use the LDA parametrization due to Vosko et al. (VWN) [9]. The core is taken as full which means that an all electron calculation is carried out, and a cutoff radius of 5 Å was used. The forces are calculated using rigorous formal derivatives of the expression for the energy in the Harris functional, as discussed by Lin and Harris [4]. The interface software used to construct the models and obtain their RDFs was CERIUS2.

3. Results and discussion

In Fig. 1 you can appreciate the smallest supercell generated that contains 32 atoms and in Fig. 2 the biggest one constructed that contains 500 atoms, both with 50% porosity. The violet[1] atoms are those that we considered to be on the pore surface. It is clear that the distortion of the silicon network for 32 atoms is notorious but not as relevant for the 500 atom supercell. In Figs. 3 and 4 you can see the RDFs for the 32 and 500 atoms models; the red curve of Fig. 3 shows the positions of the silicon atoms on the surface pore and the blue curves of Fig. 3 the positions of the other atoms in the supercell. In Fig. 4 we plotted the total RDF (blue line) since it was impossible to identify which atoms belonged to the pore and which to the backbone. The green curve in both graphs is the radial distribution function of crystalline silicon. It seems that the atoms lying on the pore surface are separated by a bigger distance than those within the volume of the supercell.
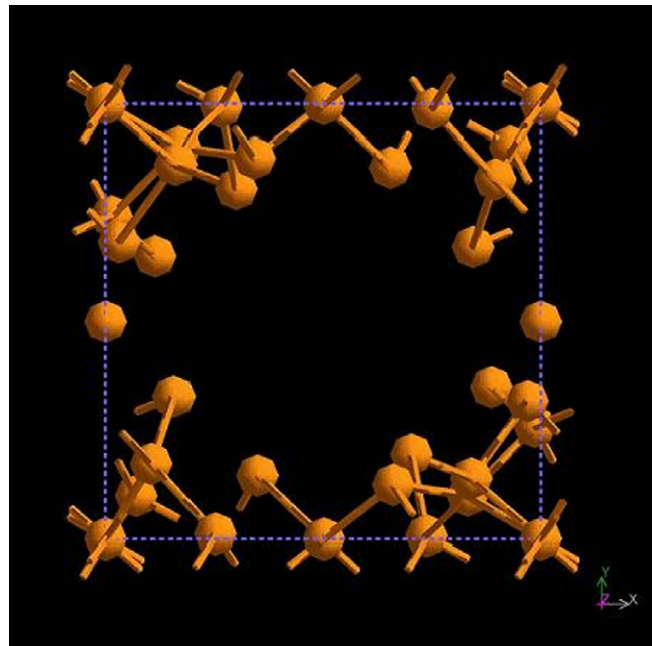

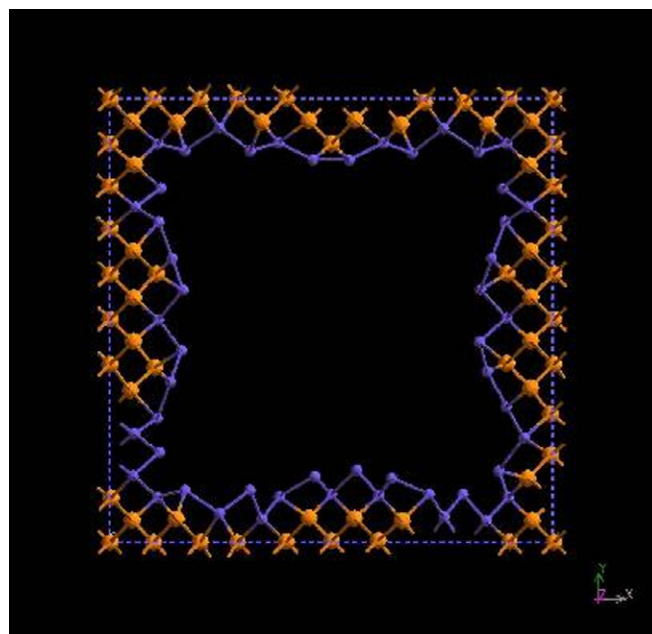Fig. 1. Silicon porous supercell with 32 atoms, 50% of porosity and relaxed.

Fig. 2. Silicon porous supercell with 500 atoms, 50% of porosity and relaxed. The violet atoms are on the pore surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Comparing Figs. 3 and 4 we can conclude that the 500 atom model presents some 'crystalline' regions and the 32 atom model, none. In Table 1 we present the positions of the first peak of the RDF of the first group of models as well as the number of atoms in the supercell. In Table 2 we show the same data but for the second group. As we can see, the interatomic distance of the nn silicon atoms

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[1] For interpretation of color in Figs. 2–4, the reader is referred to the web version of this article.
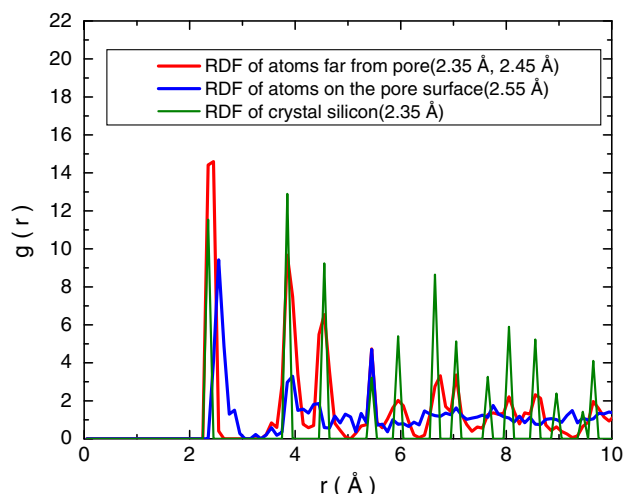
Fig. 3. Model with 32 atoms. Radial distribution function of the 32 atoms model (red curve) and the radial distribution function for crystalline silicon (green curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
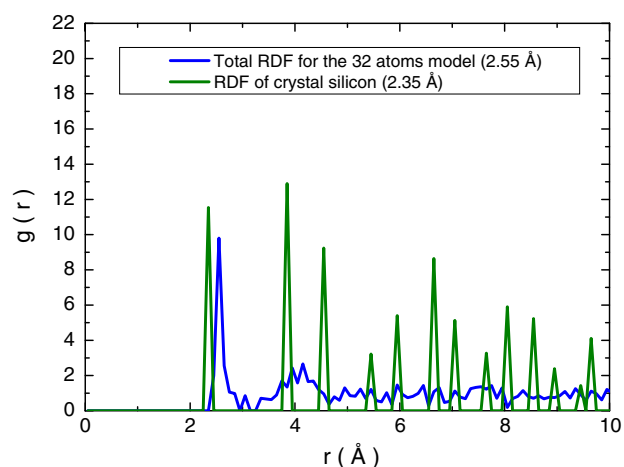

Fig. 4. Model with 500 atoms. Radial distribution functions of atoms lying on pore surface (blue) and far from pore (red). Radial distribution function for crystalline silicon (green curve). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Group 1 of models

No. atoms	Porosity (%)	Peak1 (Å)	Peak2 (Å)	Peak3 (Å)
43	80	2.55	4.05	–
87	60	2.55	3.85	5.95
107	50	2.55	4.15	6.05
129	40	2.55	4.05	–
162	25	2.55	4.05	–
168	22	2.45	4.05	7.05
173	20	2.45	3.95	6.05
183	15	2.45	3.85	4.55
190	12	2.45	3.95	4.55
192	11	2.45	3.85	4.55
194	10	2.35	3.85	4.55

Positions of the first, second and third peak of the radial distribution function. The length side of the supercell is a constant of 16.292 Å.

Table 2
Group 2 of models

No. atoms	Length side (Å)	Peak1 (Å)	Peak2 (Å)	Peak3 (Å)
32	10.850	2.55	4.15	5.25
108	16.292	2.45	4.05	–
256	21.722	2.45	3.85	6.65
500	27.150	2.45	3.85	4.45

Positions of the first, second and third peak of the radial distribution function. The porosity of the models is 50%.

increases as the porosity of the supercell increases, or as the 'thickness' of the silicon backbone decreases.

Even if we think that it is necessary to increase the number of atoms in our simulations to enable a direct comparison between our results and the experimental ones, we consider that the results here presented, show a coincidence with the experimental findings for the crystalline porous silicon topology.

4. Conclusions

For future developments in nanotechnology, it is important to keep in mind that the properties of the silicon changes not just by means of the nature of the structure considered, like porous, amorphous or porous amorphous, but also due to the size of their structures. If the human is able to manipulate silicon nanostructures, it is necessary to understand how the size of the structure will affect their topological, electronical and optical properties.

We can conclude that when the silicon backbone in the supercell is too small, even a simple relaxation of the simulation cell generates an amorphous silicon structure. On the other hand when the size of the silicon backbone is increased, the structure tends to remain 'crystalline'. The size of the backbone is a determining factor in the 'crystallinity' of the porous silicon structure.

Thinking about nanotechnology, we have to recognize that decreasing the size of the silicon structures will affect its bulky crystalline nature, and also their related properties like the electronic and optical ones.

Acknowledgments

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